MOLECULAR SIMULATIONS OF SURFACTANTS AND SILANES:
SELF-ASSEMBLY IN SOLUTIONS AND ON SURFACES, AND
FRICITION BETWEEN MONOLAYERS

by

Vivek Kapila

Copyright © Vivek Kapila 2004

A Dissertation Submitted to the Faculty of the
DEPARTMENT OF MATERIALS SCIENCE & ENGINEERING
In Partial Fulfillment of the Requirements
For the Degree of
Doctor of Philosophy
In the Graduate College
THE UNIVERSITY OF ARIZONA

2004
As members of the Final Examination Committee, we certify that we have read the dissertation prepared by Vivek Kapila entitled Molecular Simulations of Surfactants and Silanes: Self-Assembly in Solutions and on Surfaces, and Friction between Monolayers and recommend that it be accepted as fulfilling the dissertation requirement for the Degree of Doctor of Philosophy.

Pierre A. Deymier  
Sriini Raghavan  
Joseph M. Simmons  
John F. O'Hanlon  
Olgiord A. Palusinski

Final approval and acceptance of this dissertation is contingent upon the candidate's submission of the final copy of the dissertation to the Graduate College.

I hereby certify that I have read this dissertation prepared under my direction and recommend that it be accepted as fulfilling the dissertation requirement.

Dissertation Director: Pierre Deymier
STATEMENT BY AUTHOR

This dissertation has been submitted in partial fulfillment of requirements for an advanced degree at The University of Arizona and is deposited in the University Library to be made available to borrowers under rules of the Library.

Brief quotations from this dissertation are allowable without special permission, provided that accurate acknowledgment of source is made. Requests for permission for extended quotation from or reproduction of this manuscript in whole or in part may be granted by the copyright holder.

SIGNED: Vivek Kapila
ACKNOWLEDGEMENTS

As this dissertation is coming to its successful fruition, I feel a strong urge to pause for a moment, and acknowledge those who have made their own special contribution in bringing this work to its desired result. I would like to first acknowledge the role my advisor, Prof. Pierre Deymier, has played in this work. Dr. Deymier has been of tremendous help in turning me from a complete novice in computer programming and molecular simulations to an active student of the subject by spending countless hours with me teaching the very nuances of Monte Carlo and molecular dynamics simulations. His contributions have not only been limited to the task of teaching, but also in taking a keen interest in seeing that I do not falter and fall apart because of any weak moments in my life.

I would also like to acknowledge the role of Prof. Srini Raghavan in this dissertation, who actually hired me as a graduate student to work on the simulations component of this project. I thank him for his teaching in surface chemistry, very crucial contributions in the publications of results during the course of this work, and also for providing me the opportunities to work in his lab at AML and exposing me to the wonderful micro-world of MEMS. I have also been to many of the dinner parties he hosted for his group at his home. The one thing I would regret the most is that I perhaps was not able to take the full advantage of his wealth of knowledge as I failed to meet him on a more regular basis.

I am grateful to Prof. Joseph Simmons for accepting to serve on my dissertation committee on a very short notice. He has also been very generous in providing me the much-needed pointers in my job search. I am also grateful to Dr. Brian Zelinski for providing me the much-needed financial support in the form of teaching assistantships for over half the duration of this work. Thanks are also due to Dr. Dunbar Birnie for his services as my major committee member during my oral qualifying exam.

Next, I would like to thank my minor committee members Dr. John O'Hanlon, Dr. John L. Prince, and Dr. O. Palusinski. I am indebted to Dr. O'Hanlon for taking time out of his retirement to serve both on my oral qualifying exam and the final dissertation defense. I would also like to thank Dr. O'Hanlon for his teachings in semiconductor processing, and vacuum science classes. I also learnt from Dr. O'Hanlon a novel way of educating and learning, i.e., receiving individual queries from students in the e-mail and then distributing the answers to the entire class.

So many years have passed since I graduated with my Bachelor's degree in Metallurgical Engineering from the University of Roorkee (now an IIT), India in 1996. It's time that I acknowledge the contributions of the individuals, namely, Dr. R.P. Ram, Dr. S. Prakash, Dr. V.K. Tewari, and Dr. S.K. Patwardhan, who encouraged and provided me every help in my pursuit for higher studies. My undergraduate research project advisor Dr. R.P. Ram deserves special mention for the many hours he spent in troubleshooting my experiments during that work. Next, I would also like to thank my masters thesis advisor Dr. Jon J. Kellar for giving me an opportunity to work in his group and to encourage me to pursue the doctoral degree at the University of Arizona. He still continues to guide me and is always available for help.
Many thanks are due to Ms. Janna M. Harris for her help during the early years of the project in the MC simulations of the surfactant. I would also like to thank Dr. Marcia Almanza-Workman, and Dr. Wayne Huang for their help in making me understand the experimental aspects of the project. Many thanks are due to Mr. Vasseline Petrov for his help in making animations from my MD simulation data. I would also like to thank my colleagues Mr. Krishna Muralidharan, Dr. Kidong Oh, and Dr. F.J. Cherne (now at Los Alamos National Labs) for the many useful discussions of molecular dynamics simulations during the course of this work. I am also grateful to Dr. Steve Valone and Dr. Alejandro Stratchan at the Los Alamos National Laboratories for enhancing my understanding of MD simulations of polymers during my internship there. Thanks are also due to Mr. Haripin Chandra, Mr. Siddhartha Kondoju, and Ms. Sri Rajagopalan for running some of my codes on their computers during the last stages of the work.

As I remember the contributions of many in shaping my life, I feel I am most influenced by my family. My parents, Mr. Satish Kumar Kapila and Mrs. Sunita Kapila, have provided me the best possible schooling, and an environment conducive to learning at home. They have sacrificed their parental love many a times in seeing that I, and also both of my brothers are able to choose the careers of our choice. One of the persons I have been most influenced right from my childhood is my brother, Dr. Vikram Kapila. He removed the fears of math and science from my mind at an early age and directed me towards a career in engineering. He is still doing so very wonderfully as a Professor at the Polytechnic University in Brooklyn, New York, teaching his students in Aerospace and Mechanical Engineering. My brother, Mr. Manoj Kumar Kapila, has also influenced my life in instilling in me the philosophy that "tough times never last, but tough people do". I must also thank a very special person in my life, my better half, Ms. Kanthimani Padmanabhan, who has become an epitome of patience now, waiting all these five years for me to start a new chapter in our lives together.

Last, but not the least there is a long list of friends and acquaintances who have been instrumental in seeing me through to this day. The list includes, Mr. Hamidul Haque, Mr. Ashish Mittal, Mr. Anurag Trivedi, Mr. Shishir Kant, Mr. Ravindra Kharde, Mr. Rabindra Bhattarai, Mr. Sanjib Sharma, Mr. Rajesh Sekhar, Mr. Mahesh Khandeparker, Mr. Ananth Kini, and Mr. Siddhartha Panwar.
DEDICATION

This work is dedicated to the love and support of my parents
# TABLE OF CONTENTS

LIST OF ILLUSTRATIONS ........................................................................ 9

LIST OF TABLES ............................................................................... 13

ABSTRACT ....................................................................................... 14

1 INTRODUCTION ............................................................................. 15

1.1 Background .................................................................................. 21

1.1.1 Stiction and friction in MEMS .................................................. 21

1.1.2 Simulations of surfactant solutions ........................................... 27

1.1.3 Molecular dynamics simulations of friction .............................. 31

2 MODELS AND SIMULATION METHODOLOGIES ....................... 34

2.1 Stochastic simulations ................................................................. 35

2.1.1 Canonical Monte Carlo .......................................................... 35

2.1.2 Lattice models ....................................................................... 40

2.1.3 Monte Carlo moves ................................................................. 42

2.1.4 Configurational Bias Monte Carlo .......................................... 45

2.2 Deterministic methods ............................................................... 53

2.2.1 Microcanonical molecular dynamics ...................................... 53

2.2.2 Periodic boundary conditions ............................................... 54

2.2.3 Integration methods ............................................................... 56

2.2.4 Canonical ensemble molecular dynamics ............................... 61

2.2.5 Interatomic potentials ............................................................ 63

3 SURFACTANTS IN SOLUTIONS: MODELING INTERACTION BETWEEN HEAD GROUPS FOR SURFACTANT SELF-ASSEMBLY ........................................................................ 69

3.1 Models and Methods ................................................................... 72

3.2 Results and Discussion ............................................................... 78

3.2.1 Simulation Results ................................................................. 78

3.2.1.1 Monomer concentration as a function of overall surfactant concentration ............................................ 83

3.2.1.2 Energy per surfactant chain as a function of overall surfactant concentration ........................................... 83

3.2.1.3 CMC from Cluster Size Distributions .................................. 88

3.2.2 Discussion of MC results ......................................................... 92

3.3 Conclusions ............................................................................... 103
# 4 SELF-ASSEMBLY OF CATIONIC AND NON-IONIC ALKYLSILANES ON A CHARGED SUBSTRATE

4.1 Models and Methods ................................................................. 109
4.2 Results and Discussion ................................................................. 116
4.3 Conclusions .................................................................................... 131

# 5 MOLECULAR DYNAMICS SIMULATION OF FRICTION BETWEEN ALKYLSILANE MONOLAYERS

5.1 Model .............................................................................................. 135
5.2 Results ............................................................................................ 141
  5.2.1 Compression of alkylsilane films .................................................. 144
  5.2.2 Sliding friction as a function of separation between the films .......... 146
  5.2.3 Friction as a function of temperature ........................................... 150
  5.2.4 Friction as a function of substrate velocity .................................... 155
5.3 Conclusions ..................................................................................... 159

# 6 SUMMARY AND RECOMMENDATIONS FOR THE FUTURE WORK

REFERENCES ....................................................................................... 168
LIST OF ILLUSTRATIONS

Figure 1.1 An illustration of basic steps employed in fabrication of MEMS, (a) Silicon substrate with sacrificial oxide layer, (b) patterning, (c) deposition of a polysilicon structural layer, (d) etching of sacrificial oxide layer. .......................... 22

Figure 2.1 Flow chart of Metropolis MC method. ............................................................................ 39

Figure 2.2 (a) original configuration of a lattice chain; configuration after, (b) reptation MC move, (c) flip MC move, (d) chain translation MC move........... 43

Figure 2.3 An illustration of chain growth on a two dimensional lattice, (a) "blind" random walk in conventional MC, (b) self-avoiding walk in Rosenbluth-Rosenbluth method. ........................................................................... 47

Figure 2.4 Possible configurations of a chain molecule with 5 segments in two-dimensions. ................................................................. 49

Figure 2.5 An illustration of roulette wheel algorithm method for selection of sites in a configurational-bias MC. ........................................................................... 52

Figure 2.6 A schematic representation of periodic boundary conditions in 2D............. 55

Figure 2.7 An illustration of (a) bond stretching, and (b) bond bending. ....................... 66

Figure 2.8 The Lennard Jones potential ................................................................. 68

Figure 3.1 Energy per chain as a function of grid size at different surfactant concentrations. ................................................................................. 77

Figure 3.2 Concentration of monomers versus overall surfactant concentration in the LR model. ........................................................................... 79

Figure 3.3 Concentration of monomers versus overall surfactant concentration in the LHG model. ........................................................................... 80

Figure 3.4 Monomer concentration as a function of overall surfactant concentration in SLR model................................. 81

Figure 3.5 Concentration of monomers as a function of overall surfactant concentration in SR model.................. 83
LIST OF ILLUSTRATIONS- Continued

Figure 3.6  Energy/surfactant chain as a function of overall surfactant concentration in LR model. ................................................................. 84

Figure 3.7  Energy/surfactant chain as a function of overall surfactant concentration in the LHG model. .................................................. 85

Figure 3.8  Energy/surfactant chain as a function of overall surfactant concentration in the SLR model. .................................................... 86

Figure 3.9  Energy/surfactant chain as a function of overall surfactant concentration in the SR model..................................................... 87

Figure 3.10  A representative cluster size distribution at a (low) concentration of 7.39 x 10^-4 in LR, SLR, and LHG models. The inset shows cluster size distributions in SR model at a concentration of 2.02 x 10^3 in the SLR model (inset). ....................................................... 88

Figure 3.11  Representative cluster size distributions in LR and LHG models at a (high) concentration of 5.18 x 10^3 and at a concentration of 4.36 x 10^3 in SR and SLR models. The inset shows cluster size distributions in the SR model at large cluster sizes. .............................................................. 89

Figure 3.12  All possible configurations of an isolated chain molecule on a 2-D lattice...... 97

Figure 3.13  Possible configurations of a two chain molecule system when the head groups of these molecules are nearest neighbor and configuration of one chain molecule is fixed. ................................................................. 99

Figure 3.14  Illustration of steric repulsive interaction between the surfactant head groups as a function of distance between the constrained first head groups of the pair of surfactant chains.................................................................. 100

Figure 4.1  An illustration of (a) non-ionic alkylsilane, and (b) cationic alkylsilane. ...... 110

Figure 4.2  Snapshots of the (a) non-ionic, and (b) silane films following rinsing and relaxation........................................................................... 119

Figure 4.3  Tail group distribution profiles in non-ionic/cationic alkylsilane films as a function of distance from surface............................................. 120
LIST OF ILLUSTRATIONS - Continued

Figure 4.4 (a) sample HH correlations for a layer completely occupied by head groups, (b) sample HH and HT correlations for a layer occupied by head and tail groups in an ordered form................................................................. 123

Figure 4.5 (a) The HH, HW and HT correlations in non-ionic silane on layer 1, (b) the HH, HW, HT and HI correlations in ionic-silane on layer1........................................... 125

Figure 4.6 TT, TW, and TI correlations in cationic alkylsilane on (a) layer2, (b) layer 3, (c) layer 4, (d) layer 5, (e) layer 6, (f) layer 7, (g) layer 8, and (h) layer 9 of the film................................................................. 128

Figure 4.7 A simplified representation of water pores in cationic alkylsilane film .......... 129

Figure 4.8 TT and TW correlations in non-ionic alkylsilane on (a) layer 2, (b) layer 3, (c) layer 4, (d) layer 5, (e) layer 6, (f) layer 7, (g) layer 8, and (h) layer 9 of the film................................................................. 130

Figure 4.9 A simplified representation of water pores in the non-ionic alkylsilane film.. 131

Figure 5.1 A representation of α-cristobalite substrate. The red atoms represent O and the yellow atoms represent Si ................................................................. 136

Figure 5.2 A simplified representation of experimental alkylsilane films on a silica substrate................................................................. 137

Figure 5.3 A schematic representation of the initial structure of the alkylsilane films on α-cristobalite substrates used in the friction simulations................................. 138

Figure 5.4 Instantaneous normal force on the films during compression at a rate of 2 Å/ps as a function of MD time steps, one time step corresponds to 1fs .......... 146

Figure 5.5 Friction coefficient as a function of normal force................................................................. 149

Figure 5.6 Friction force as a function of normal force on the films................................................................. 149

Figure 5.7 Variation of friction coefficient as a function of temperature................................. 151

Figure 5.8 Friction force as a function of temperature................................................................. 151

Figure 5.9 Normal force on the films as a function of temperature................................................................. 152

Figure 5.10 Friction coefficient as a function of substrate velocity................................................................. 156
LIST OF ILLUSTRATIONS - Continued

Figure 5.11  Normal load as a function of shear rate. ............................................. 156
Figure 5.12  Friction force as a function of shear rate. ............................................. 157
LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Gear corrector coefficients [70]</td>
<td>60</td>
</tr>
<tr>
<td>3.1</td>
<td>Summary of surfactant chain structures and nature of HH interactions in various models</td>
<td>73</td>
</tr>
<tr>
<td>3.2</td>
<td>Summary of CMC values in LR and LHS models</td>
<td>91</td>
</tr>
<tr>
<td>4.1</td>
<td>Summary of interaction energies for various pair interactions in the non-ionic and cationic alkylsilane models</td>
<td>113</td>
</tr>
<tr>
<td>4.2</td>
<td>Number concentration of alkylsilane chains on the surface before and after rinsing</td>
<td>118</td>
</tr>
<tr>
<td>5.1</td>
<td>Parameters for harmonic bond stretching and bond bending potentials, and LJ interactions</td>
<td>139</td>
</tr>
<tr>
<td>5.2</td>
<td>Normal load, frictional force and friction coefficients as a function of separation between films</td>
<td>148</td>
</tr>
<tr>
<td>5.3</td>
<td>Normal load, friction force, and friction coefficient as a function of temperature</td>
<td>150</td>
</tr>
<tr>
<td>5.4</td>
<td>Shear force, normal load, and friction coefficients as a function of substrate velocity</td>
<td>155</td>
</tr>
</tbody>
</table>
ABSTRACT

Recent experimental efforts have focused on the development of water-based chemistries to deposit hydrophobic alkylsilane films on the silica surfaces to address the problem of stiction induced failure in MEMS. A detailed molecular level examination of the structure of these films is limited with the available experimental methods. Therefore, this work undertakes an investigation of the structure and properties of self-assembled alkylsilane monolayer films via Monte Carlo (MC), and molecular dynamics (MD) simulations. The existing literature on the surfactant aggregation is used as a guide for modeling the alkylsilanes molecules. However, the current literature is ambiguous whether to describe interactions between the surfactant head groups as short-range or long-range. This work resolves this discrepancy successfully by performing a series of simulations of various structural and interaction models of surfactants. Simulations show that a realistic surfactant aggregation requires an excluded volume of the head groups, necessitating different interaction models in different structural models of surfactants. Next, MC simulations have been used to investigate the impact of the charged group in cationic alkylsilane on the structure of the deposited film. The structure of the films is characterized with the spatial pair correlations at each molecular layer of the deposited films. The long-range correlations are seen for the films of cationic alkylsilanes. Also, the frictional behavior of the alkylsilane films deposited on silica substrates is examined via molecular dynamics simulations. The friction coefficients of the films are obtained as a function of separation between the films, temperature, and velocity of the substrates. The results of the MD simulations support a thermal activation model of friction.
1 INTRODUCTION

Silicon has long been known for its spectacular electronic properties. Recently, its mechanical properties have also received attention and it has become a material of choice for some of the tiniest structures of technical importance being manufactured today, called microelectromechanical systems, or MEMS [1]. A lot of effort is being spent these days for the manufacturing of silicon based micro-sensors and micro-actuators. One of the most commonly used approaches in the fabrication of MEMS devices is known as surface micromachining. The device structures in surface micromachining method are fabricated by the deposition, patterning, and etching of various levels of materials layers. Similar processing steps have long been used in the microelectronic industry for the chip manufacturing. Surface micromachining, therefore, is benefited a lot from the existing infrastructure, and the advances made in the microelectronic fabrication. The microstructures of interest are obtained, in a surface micromachining process, by removing a surrounding sacrificial oxide layer in a liquid phase HF or a buffered HF etch, followed by rinsing and drying [2]. The microstructures thus released are prone to sticking to the substrate due to very strong interfacial forces, such as, capillary, van der Walls, and electrostatic attractions between the wet, hydrophilic polysilicon surfaces [3-5], causing failure of the device. This phenomenon is often termed ‘stiction’. Stiction can take place both during wet-etch processing, referred to as ‘after-rinse stiction’, or during use in an environment of changing humidity, referred to as ‘in-use stiction’.
Despite years of advancement in surface micro-machining technologies, stiction of microstructures remains a fundamental problem in MEMS fabrication. Various techniques have been suggested to eliminate the stiction problem in the MEMS, of which, coating the microstructure surfaces with a hydrophobic self-assembled monolayer (SAM) being the most popular [4-9]. Traditionally, a long chain alkylsilane is deposited on the hydrophilic surfaces from an organic solution. Increasing concerns regarding organic wastes in work places have also led to the development of novel chemistries for deposition of hydrophobic monolayers from water-based solutions [10, 11]. The deposition of alkylsilane from the aqueous solutions is usually complicated because of poor stability of silane in the aqueous environment. Problem of silane stability in aqueous medium is sometimes addressed by utilizing a mixed solution of a cationic surfactant and an alkylsilane in which cationic surfactants prevents bulk polymerization of silane molecules. Also, commercially available, water dispersible cationic and non-ionic silanes have been used recently to deposit highly hydrophobic coatings on polysilicon surfaces [12-14].

Besides stiction, friction is a major concern in the operation of those MEMS devices that have components (motors, gears, etc.) with moving surfaces in contact. These surfaces undergo friction resulting in wear debris detrimental to the operation of MEMS devices [15]. In order to minimize such losses, duplex wear resistant and anti-stiction coatings have been proposed in which a tungsten oxide coating is first applied to the exposed surfaces from an aqueous based precursor solution and then an alkylsilane
coating is applied over tungsten oxide. Tungsten coating minimizes friction losses because of its superior wear properties [15] whereas silane coating provides anti-stiction properties.

Because of their role in the development of environmentally acceptable methodologies, aqueous surfactant and silane solutions are systems of extreme technological importance. The coatings deposited on the MEMS systems are roughly a monolayer (or a few monolayers) thick. It is, therefore, imperative to understand the underlying physics and chemistry of these systems at the molecular level for enhancements in the coating methods and quality. However, existing experimental methods and tools are still limited in their scope to investigate the material systems in sufficient detail at the length and time scales involved in the deposition of silane monolayers on MEMS surfaces.

Atomistic simulation techniques such as Monte Carlo (MC) and molecular dynamics (MD) are now well-established tools in the studies of materials at the atomic and molecular level. MD and MC methods find their origin in classical statistical mechanics [16]. Provided a model for the interactions between the atomic constituents of some system exists (for instance, in the form of interatomic or intermolecular potentials which describe the energy of the system as a function of its microscopic degrees of freedom), one can sample deterministically (MD) or stochastically (MC) the microscopic states of the system. The microscopic degrees of freedom usually consist of the set of positions
and momenta of the particles. The original intent of MD and MC is, once equilibrium is achieved, to use the concepts of temporal averaging (MD) [17] or statistical averaging (MC) [18] over the sampled microscopic states to calculate the properties of a macroscopic system. In addition to determination of equilibrium properties, MD methods are also used to study non-equilibrium system properties.

The length and time scales involved in the molecular level investigation of structure of alkylsilane monolayers and its evolution under sliding friction conditions are relevant to molecular simulations. Therefore, there is a significant motivation for studying these systems via MC and MD simulations. The objectives of this work are to examine, via molecular simulations, the structure of self-assembled cationic and non-ionic silane films on a charged polysilicon substrate and effect of sliding friction on these monolayers.

The equilibrium structures of alkylsilane films in this work are generated and examined by MC simulations. As will be discussed in chapter 2, MC simulations are stochastic in nature and depend only on probabilities. These methods allow calculation of equilibrium thermodynamic properties without following real dynamics of the system. MC simulations utilize artificial, time-independent moves to generate a large number of states of a system in equilibrium. A statistical average of the time-independent system properties over the large number of states generated by MC simulation provides a reliable estimate of these properties. The time dependent properties, however, can only be calculated by following the evolution of a system in real time. This is done in a MD
simulation by solving equations of motions (chapter 2) of a collection of particles making up the system. Friction is a (non-equilibrium) dynamic process. MD simulations are, therefore, used for investigating the effect of friction on pre-assembled alkylsilane monolayers anchored to silicon substrates. An overview of these two simulation methods (MC and MD) is provided in chapter 2.

Success of any simulation study depends on the development of an adequate structural model of the system and determination of appropriate interaction parameters between various groups. Such information can often be found in the literature and can be used in the study of the specific system. However, few MC simulation studies of alkylsilane are available in the literature. In contrast, numerous MC and MD studies of, structurally similar, surfactant molecules have been reported in the literature. Surfactants are similar to alkylsilanes in that they both have a hydrophobic tail with a hydrocarbon backbone. This structural similarity in alkylsilane and surfactant molecules is utilized in this work for developing interaction models for the groups in the hydrophobic tails of alkylsilane. The potential model for the interactions between various chemical groups in alkylsilanes is based on the interactions used in an acceptable potential model for surfactants. An acceptable potential model for surfactants here means a model whose simulated behavior is similar to the behavior of an experimental surfactant system. Numerous simulations studies of surfactants describe models that reproduce the behavior seen in experiments. However, these studies are ambiguous with regard to the modeling of interactions between the head groups of surfactants. It, therefore, necessitated, a detailed study of the
effect of interactions between the head groups on surfactant self-assembly. The results and a discussion of this work are presented in chapter 3.

In Chapter 4, a study of self-assembly of alkylsilane monolayers on a charged substrate is presented. As discussed above, the alkysilane model used in this work is based on the surfactant model developed in chapter 3. Although alkysilane and surfactant molecules are structurally similar with regard to their hydrocarbon tails, the nature of the head groups in these two molecules is different. While alkysilane head groups are reactive and undergo a polymerization reaction, surfactant head groups repel each other. Therefore, interaction parameters for alkysilane head groups differ from those used in surfactant model and are determined separately. The alkysilane models are then used to study the effect of the presence of a charged group in the alkysilane chain on the structure of the self-assembled films. The structure of self-assembled films obtained from simulations is then compared with the hydrophobicity and porosity observed in experimentally deposited self-assembled films of cationic and non-ionic alkysilanes.

Chapter 5 investigates the effect of friction on the alkysilane films anchored to a silica (α-cristobalite) substrate. The frictional behavior of the alkysilane films is determined as a function of separation between the films, temperature and also the sliding velocity of substrates. A summary of this dissertation work is provided in chapter 6 along with the recommendations for the future work.
1.1 Background

A review of literature is given in section 1.1.1 to describe MEMS fabrication process and introduce the problem of stiction and friction in MEMS. Section 1.1.2 presents a review of literature on MC and MD studies of surfactant and silane self-assembly in solutions and on surfaces. Finally, in section 1.1.3, a review of MD studies of friction of monolayers is given.

1.1.1 Stiction and friction in MEMS

Recent years have seen a growing interest in developing technologies that use silicon as a mechanical material. The standard processes of the integrated circuit industry have successfully been applied to the fabrication of miniature mechanical components (micromachines) such as membranes, gears, motors, pumps, and valves [2]. The integration of miniaturized mechanical components has spawned a new technology, known as microelectromechanical systems (MEMS). It promises to extend the benefits of microelectronic fabrication to sensing and actuating functions. A number of fabrication techniques have been developed for this technology; of which surface micromachining is one of the most popular one [1].

Surface micromachining, defined as the fabrication of microelectromechanical structures from the deposited thin films, is one of the core technological processes
underlying MEMS. Surface microstructures have lateral dimensions 50-500 microns, with a thickness of 0.1-2.5 microns, and are offset 0.1-2 microns from the substrate.

The basic steps used in a surface micromachining process are illustrated in Fig. 1.1. First the substrate is typically coated with a sacrificial oxide layer (Fig. 1.1 a). Next, this oxide layer is patterned (Figure 1.1 b). The microstructure thin film is then deposited and etched (Fig. 1.1 c). Finally, selective etching of the sacrificial layer creates freestanding micromechanical structures such as the cantilever beam shown in cross section in Fig. 1.1 d. The technique can be extended to make multiple layer microstructures.

Figure 1.1 An illustration of basic steps employed in fabrication of MEMS, (a) Silicon substrate with sacrificial oxide layer, (b) patterning, (c) deposition of a polysilicon structural layer, (d) etching of sacrificial oxide layer.
Polysilicon microstructures are an important example of structures fabricated by a surface micromachining process. The mechanical properties of silicon make it an excellent material for micromachining. Surface micromachining has rapidly expanded owing, in part, to the mature infrastructure for depositing, patterning, and etching thin films borrowed from silicon integrated circuit technology. Another reason for this rapid expansion has been the potential of integrated micro-systems, which incorporate surface micromachined sensors or actuators together with integrated electronics on the same substrate [19].

Given the large surface area to volume ratio of surface microstructures, they are particularly vulnerable to sticking to the substrate or adjacent microstructures during the release process or later, during use [3]. This phenomenon is more generally called stiction. Adhesion failure can occur in two ways: after-rinse stiction, and in-use stiction. After-rinse stiction occurs after the sacrificial release of the microstructures where the surface tension of the rinse liquid is sufficiently strong to pull the suspending microstructures, e.g. the cantilevered beam in Fig. 1.1, in contact with the substrate, leading to permanent adhesion. In-use stiction can occur when a microstructure is exposed to an environment of changing humidity. If the microstructure is first exposed to a humid environment, water vapor can condense to form water droplets in narrow gaps present between surfaces brought into contact. This capillary condensation phenomenon can occur during the normal device operation of micro-devices. If the surfaces of the microstructures are hydrophilic, the water droplets exert an attractive force pulling the
microstructure toward the substrate. When the microstructure is next exposed to a dry environment, as the water droplets evaporate, the attractive force increases (due to the reduced gap) causing the eventual collapse and permanent adhesion of the microstructures [5].

Various techniques have been suggested for the elimination of after-rinse stiction and in-use stiction in surface micro-machined structures, such as, freeze sublimation [20], super critical drying [21], use of dimples and sharp corners [22], and hydrophobic coatings [4, 12-14]. Freeze sublimation and super-critical drying have been successful in taking care of the after-rinse stiction problem by eliminating the formation of concave meniscus underneath the released microstructure. However, these techniques have failed to address the in-use stiction problem. The in-use stiction problem is solved by surface modification by either using surface bumps (to reduce the area between contacting surfaces) or by forming hydrophobic films on the surface.

Deposition of hydrophobic self-assembled monolayer (SAM) films is one of the most successful approaches to chemical modification of silicon surfaces in order to reduce adhesion in microstructures. By making the surface hydrophobic, the capillary attraction that collapses the microstructures when the surfaces are hydrophilic is greatly reduced. As a result, microstructures come out of the final water rinse extremely dry. Also, hydrophobic films eliminate in-use stiction by avoiding the formation of water layers on the surface, thereby, eliminating the capillary forces during the operation of the device.
Additionally, absence of hydrophilic hydroxy groups on the surface eliminates the possibility of hydrogen bonding as the two surfaces come in contact.

A typical sequence of the steps used in the existing techniques for the deposition of hydrophobic films on the polysilicon surfaces, however, requires the use of several organic solvents and results in organic and aqueous wastes [8]. Also, high quality SAMs of alkyltrichlorosilane derivatives are not easy to form, mainly because of the need to carefully control the amount of water in the liquid medium used for deposition [23-26]. While incomplete monolayers are formed in the absence of water, excess water results in polymerization of silanes in solution and polysiloxane deposition of the surface [27].

Despite some of its excellent mechanical properties, silicon, unfortunately, has poor tribological properties [28] and practical MEMS devices must be designed to overcome these limitations. Rotating devices such as pinwheels and microturbines have been fabricated with the current technology. However, their useful life is rendered very short as they are frequently subject to stiction problems preventing startup [29] or wear related failure [28] after a few minutes of operation creating surface contamination. The short functional life of these devices is attributed to the excessive wear rate of silicon induced by high friction and low cohesive energy density of the material [30-32]. Since silicon micromachining is such a well-established technology, the most logical solution is to leave the silicon micromachining in place, but devise methods of improving or modifying the surface properties of silicon and polysilicon.
Several studies have been conducted to develop solid and liquid lubricants and hard films to minimize friction and wear. The use of tungsten films as wear resistant coatings for silicon based MEMS has been investigated by Mani et al [15] and Dugger [33]. Their approach was to first release the structures in HF, rinse in water and then air dry (allowing stiction to occur). The wafer was transferred to a chemical vapor deposition (CVD) tool, where any surface oxide was removed in-situ and tungsten was deposited using WF$_6$ plasma at high temperature. “Stuck” beams were released during the deposition process. Using a sidewall tribometer, these authors measured the friction coefficient as a function of oscillatory cycles and found it to remain low and consistent for two weeks in humid air. X-ray photoelectron spectroscopy measurements of the composition of the tungsten coated surfaces indicated that after 14 days exposure to air (the time after which these experiments were run), the surface contained about 33 atomic percent oxygen and 17 percent W (as WO$_3$), 28 percent carbon, and the balance was nitrogen and fluorine. From these tests they concluded that the oxide and the large amount of adsorbed carbon governed the tribological behavior of tungsten coatings.

Friction and wear studies of self-assembled monolayer films has been done using pin on disk technique and friction force microscopy (FFM). Pin on disk [34] are macroscale friction experiments that cannot provide insight into the actual contact phenomena encountered at MEMS interfaces. Macroscopic samples with different morphologies than their microscale counter parts can obscure the importance of intrinsic surface forces, and the tribology of the macrosystem may be dominated by particulate contamination [35].
AFM [36-38] has been used to study adhesion, friction and wear properties of SAM coatings at load levels that are encountered in the operation of MEMS.

Early research by DePalma [34], Ando [39] and Ruhe [40] showed that self-assembled monolayers of alkylsilanes could be used as lubricants on smooth silicon surfaces. Octadecyltrichlorosilane was the most effective lubricant on silicon, followed by undecyltrichlorosilane and (tridecafluoro-1,1,2,2-tetrahydrooct-1-yl) trichlorosilane. The lifetime of alkylsilane monolayer coated silicon surfaces increased with an increase in chain length of the alkyl substituent.

1.1.2 Simulations of surfactant solutions

Surfactants are amphiphilic chain molecules consisting of a hydrophilic head group and a hydrophobic alkyl tail. When added to an aqueous medium, the hydrophilic head groups remain on the surface and the hydrophobic tails stick out into the air side of the interface. Upon increasing the concentration beyond a point where surface is saturated with surfactants, surfactant molecules must go into the aqueous medium. However, the alkyl tails in the surfactants remain unhappy in the aqueous environment due to their hydrophobic nature. Therefore, after a certain critical concentration surfactants start assembling into well-defined structures such as, spheres, cylinders, bilayers, etc. so as to prevent interactions of hydrophobic tails with the surrounding aqueous medium. This is also accompanied by a sharp change in the slope of solution properties when plotted
against increasing surfactant concentration. These self-assembled structures are known as micelles, and the concentration at which micellization takes place is referred to as critical micelle concentration (CMC).

Numerous Monte Carlo (MC) and molecular dynamics (MD) simulations have been used successfully in the past to study the chemical systems and the self-assembled monolayers comprising surfactant molecules. First simulations of these long chain molecules dealt with the studies of pre-assembled or self-assembled micellar structures in aqueous or organic solutions via lattice MC simulations. In lattice MC simulations, a surfactant molecule is represented as a chain of chemical groups occupying certain connected grid sites on a two or three-dimensional lattice. Extensive work has been done by Larson [41-45] showing that surfactant self-assembly can be achieved by MC simulations without having to resort to any pre-assembled micellar structure. Most of Larson’s work has focused on three-component amphiphile-oil-water systems and MC simulations were successful in making quantitative predictions of the phase behavior in these systems. By performing his simulations at different conditions of temperatures and concentrations, Larson has shown the ability of these models to predict self-assembly into lamellar, packed cylindrical, and spherical phases as well as bicontinuous structures.

Several MC studies have been carried out for the measurement of the micellar properties, such as, critical micelle concentration (CMC), micellar size, micelle shape, aggregation number, polydispersity, etc. Care and co-workers [46-48] have studied both
two dimensional and three dimensional lattice models of binary mixtures of water-surfactant systems in a canonical ensemble. The cluster size distributions have been determined as a function of temperature and concentration. The cluster size distributions show a significant polydispersity and a peak in these distributions is taken as indicative of micelle formation.

More recently, lattice surfactant systems were studied by grand-canonical MC (together with histogram-reweighting) techniques [49]. These simulations investigate amphiphilic molecules of both symmetric and asymmetric architectures. The osmotic pressure and chemical potentials/volume relationships are determined as a function of temperature. The CMC is then determined as a function of temperature from the osmotic pressure curve.

MC simulations of a three-dimensional lattice model of an amphiphile-solvent system have been presented and examined by Talsania et al [50] for their effectiveness in predicting the thermodynamics of self-association of amphiphiles in solution. MC simulations have also been used by this group for studying the solubilization of solute molecules in surfactant aggregates [51]. The effect of the ratio of head group size to tail group size on micellar properties has also been investigated.

MC simulations have been used to study the self-assembly of model surfactants on hydrophilic [52] and hydrophobic surfaces [53], and also self-assembly of alkanethiol on
Au(111) [54]. These simulations have provided the phase and structural behavior of the model system as a function of temperature, coverage, and the magnitude of surface corrugation.

MD simulations have successfully been used to study the morphology of monolayers of the cationic surfactant cetyltrimethylammonium bromide (C16TAB) at the interface between a hydrophobic substrate and an aqueous solution [55]. Also, dynamic properties, such as, the average orientation angle of the hydrophobic chains of monododecyl pentaethylene glycol (C12E5) monolayers have been investigated at the water surface using MD technique [56].

Simulations have also been used as means for proposing the mechanisms of the surfactant adsorption and aggregation using simple description of molecules and interfaces [57]. The models based on harmonic potentials and the LJ potentials have been shown to capture, at least qualitatively, the basic characteristics of water/solid interfaces and micellar solutions, and how they are influenced by the concentration and structure of surfactant molecules [57].

Zhang et al. [58] used molecular mechanics and molecular dynamics simulations to find the optimal packing structure of C18 alkyl monolayers on a Si (111) surface. The force fields used for the alkyl/Si (111) system were verified by ab initio quantum chemical calculations. It was shown that the optimal packing structure was size-
independent when it was extended to large systems. Also, an investigation of alkylsilane monolayers on silica surface has been reported, recently [59].

1.1.3 Molecular dynamics simulations of friction

Computer simulations play a critical role in understanding tribological processes. Unlike laboratory experiments, the computer simulations enable the analysis of friction/wear problem at the atomic scale. Tremendous advances in computing hardware and methodology have enabled a number of computational studies [60-67] over the last decade to study the tribological process.

MD simulations have been carried out on a number of systems of interest to wear resistant coatings. Wenning et al. [60] studied the effect of surface curvature on the law relating frictional forces with normal load as a function of surface symmetry, adhesion and contamination. MD simulations have proven useful in gaining a better understanding of the atomic stick-slip phenomenon commonly observed in the surface measurements using atomic force microscopy [61]. The friction behavior of confined thin liquid thin films under shear has been investigated as a function of molecular chain length [62]. In the MD simulations, a linear alkane film, with a variable chain length, was confined between a base and a moving wall. The simulations predicted that under low pressure, interlayer slips within the film appear in longer chains and shear stress is dependent on chain length. An MD study of model diamond-copper sliding system revealed that wear
and friction mechanisms involve four different regimes of deformation, namely, no-wear regime, adhering regime, ploughing regime, and the cutting regime [63].

The friction and wear of diamond surfaces have been investigated extensively by MD simulations [64, 65]. The tribochemical reactions occurring in two diamond surfaces in sliding contacts were simulated for both hydrogen terminated and alkyl group terminated diamond surfaces [64]. The third body effects on the friction and wear properties of diamond surfaces have been investigated [65]. Examples of third body particles include the contaminant particles between the surfaces and debris particles generated by wear of surfaces during friction. The MD simulations confirmed the experimental observations that trapped methane molecules reduce the frictional coefficient in diamond surfaces significantly [65]. The average frictional force between contacting hydrogen-terminated diamond surfaces in sliding motion has been examined as a function on applied load, crystallographic sliding direction, and the presence of chemisorbed groups on the diamond surface. The friction between diamond surfaces was shown to reduce by the chemisorption of hydrocarbon molecules. The friction properties of monolayer lubricants, chemically bound to a diamond surface, have recently been studied by Tutcin et al [66]. The role of defects in the hydrocarbon monolayers consisting of 8, 13, and 22 carbon atoms was examined on the compression, friction, and energy dissipation processes. The MD studies support the experimental observations that the number of defects present affects the energy dissipation within the films, thus affecting the measured friction. Recently, Mikulski and Harrison [67] reported the effect of packing density on the
friction of n-alkane monolayers. At high loads, significantly lower friction was observed for tightly packed monolayers, covalently bound to a diamond surface, than for a loosely packed monolayer.
2 MODELS AND SIMULATION METHODOLOGIES

In this chapter, the simulation models and methodologies used in this dissertation work are described. MC simulation methodologies are described first in section 2.1. MC simulations fall under the category of stochastic simulation methods. As the name suggests, this method relies on the probabilities of occurrence of random events. The usefulness of lattice models, in conjunction with MC methods, is highlighted in studying the time-independent material properties, such as equilibrium structure of silane films on a substrate. An introduction to the 'Metropolis method' is given which is used in the selection of random events employed by an MC simulation. This is followed by the description of MC moves used in this work.

Deterministic simulation methods (MD) are described next in section 2.2. The methodology for micro-canonical (constant N, V, E) MD is introduced. This is followed by a description of various numerical methods used in the integration of equation of motions. The Nose-Hoover thermostating method is introduced for canonical (constant N, V, T) MD simulations. This chapter ends with a description of inter-atomic potentials used in friction studies.
2.1 Stochastic simulations

2.1.1 Canonical Monte Carlo

In molecular simulations, one is interested in calculating the thermodynamic properties of a system. In an experiment, the thermodynamic properties are determined by taking averages of these properties over a period of time. In molecular simulations, these properties are calculated by invoking the *ergodic* hypothesis of classical statistical mechanics. The *ergodic* hypothesis states that the time-averaged properties are equivalent to statistical averages in an appropriate ensemble [16]. The MC methods calculate the equilibrium thermodynamic properties as statistical ensemble averages, and MD methods calculate these properties as temporal averages.

MD simulations follow the evolution of a system in real time by solving the equations of motion using a finite difference method with a suitable time step. While such an approach is required for calculating time-dependent properties such as diffusion, it may not be very well suited computationally for determining time-independent properties. This is illustrated with the following example. The time step used for integrating equations of motion in an MD simulation is approximately one to two orders of magnitude smaller than the time for the fastest motion in the simulation. In flexible molecules, such as hydrocarbon chain molecules, the highest frequency vibrations are due to bond stretching. A C-H bond vibrates with the repeat period of approximately 10 femto-seconds. If one were interested in studying a phenomenon that takes place on a
time scale of several seconds to minutes or hours, e.g., self-assembly of surfactants in solutions or alkylsilanes on surfaces, a very large number of MD steps would be needed to integrate equations of motion and to obtain reliable statistical averages of the system properties. Clearly, MD simulations of phenomena, such as surfactant and silane self-assembly will be computationally prohibitive.

An alternative approach for calculating the time-independent properties is to calculate the ensemble averages without ever attempting to simulate the real dynamics of the system. The MC simulations allow generation of a large number of states of the system stochastically and calculate the thermodynamic properties as statistical ensemble averages. Historically, the MC simulations were the first molecular simulations undertaken. Metropolis et al [18] performed the first simulations of a liquid on the MANIAC computer at Los Alamos National Laboratory.

According to statistical mechanics, any thermodynamic property \( A \) of a system can be evaluated as [68-70]

\[
<A> = \int A(\{r\}) p(\{r\}) d\{r\} \tag{2.1}
\]

where \( p(\{r\}) \) is the probability of occurrence of the configuration \( \{r\} \). This probability depends on the potential energy of the configuration \( V(\{r\}) \) and is given by,
where $\beta = 1/k_B T$, and $k_B$ is Boltzmann constant. The integrals in (2.1) and (2.2) are usually evaluated numerically.

The simple numerical methods of evaluating the above integrals, such as the trapezoidal rule or Simpson’s rule [71] are prohibitive due to the large number of calculations involved. These integrals can be evaluated more effectively by employing random sampling methods. In the simplest of these methods, the phase space (defined as a multidimensional space of positions $\{r\}$ and momenta $\{p\}$ of the particles) is explored by generating a large number of states randomly. The integrals in the equation in the equation (2.2) are then replaced by the summations as follows,

$$< A >= \frac{\sum_{i=1}^{n} A_i(\{r\}) \exp(-\beta V_i(\{r\}))}{\sum_{i=1}^{n} \exp(-\beta V_i(\{r\}))},$$

(2.3)

where $n$ is the number of randomly sampled states ‘$i$’.

Simple random sampling often generates states ‘$i$’ that do not make significant contributions to the sample averages ($\exp(-\beta V_i(\{r\}))$ very small). Metropolis et al [18] introduced the method of importance sampling that samples only the states having a Boltzmann factor ($\exp(-\beta V_i(\{r\}))$) with an appreciable value. In this method, successive
system states are generated following a Markov chain, which is defined as a series of trials in which the outcome of each trial depends only on its immediate predecessor and has no memory of the previous states. This is important as it provides a clear distinction between the MC and MD approaches. The MD simulations follow the equations of motion and are connected in time whereas the Markov chain allows unphysical moves in MC simulations and can relax the system much faster.

In practice, the importance sampling method is used frequently in the canonical ensemble (constant \( N, V, T \)). The implementation of the importance sampling method involves the generation of an initial random configuration of the system. The energy of the system in this initial configuration \( V_0 \) is calculated as a function of the positions of the particles. A new state is then generated by either a random displacement of a randomly selected particle or by a random displacement of all the particles. The energy of the new state \( V_i \) is then calculated. The transition of the system from state \( o \rightarrow i \) is always accepted if \( \Delta V = V_i - V_0 < 0 \). If the new state, \( i \), results in \( \Delta V > 0 \), then the likelihood of the new state is based on a transition probability. The transition probability is calculated as \( \exp(-\beta\Delta V) \) and a random number \( R \) is generated between 0 and 1. The new state is then accepted if the transition probability \( \exp(-\beta\Delta V) > R \). Mathematically, the acceptance probability for the new configuration in the importance sampling method is expressed as,

\[
p = \min\{1, \exp(-\beta\Delta V)\}
\] (2.4)
A flowchart for Metropolis method is illustrated in Fig. 2.1.

Figure 2.1 Flow chart of Metropolis MC method.
As with any other simulation technique, MC simulations with importance sampling also have efficiency-related issues. An algorithm is often considered to be efficient when approximately 50% of the moves are accepted. The acceptance rate of the MC moves invariably depends on the maximum displacement of the particles allowed in a step. If the maximum displacement is too small, it results in a large number of successful moves; however, the phase space is sampled very slowly. In contrast, if the maximum allowed displacement is too large, it results in high-energy overlaps and a large number of moves are rejected.

2.1.2 Lattice models

In the Lattice MC method, the physical space is discretized on a two-dimensional or a three-dimensional lattice. The atoms or molecules occupy these lattice sites and interact with each other via pair potentials. Such lattice models greatly simplify the physical description of the system and prove very useful for rapid sampling of phase space. Although the lattice models are highly simplified, they still capture in many cases the essential physics of the processes occurring at the molecular level.

Lattice based models have been used extensively for solving physical problems in a wide range of applications. For example, properties of magnetic materials can be determined by using well-known Ising model [72]. In this case the grid sites on a lattice are filled up by an up or down spin, which interact with neighboring sites as well as with a field. Several physical problems such as adsorption, absorption, and the behavior of
liquids can be modeled with a lattice gas model [72]. A lattice gas is defined as a system of $N$ molecules which are restricted to be located on one of the grid sites on a lattice, with no more than one molecule on a given grid site, and interaction between the molecules restricted to be nearest-neighbor interaction. Phase splitting and order disorder phenomena in binary liquid and solid solutions are often studied by two-component lattice gas model [72]. In such problems, each lattice site is occupied by one of the two components, which interact with nearest-neighbor potentials.

Lattice models are particularly useful in the examination of systems composed of long-chain polymer molecules. Wide ranges of time and length scales are required to adequately describe the behavior of polymers. The time scales range from approximately $10^{-14}$ s (i.e., the period of a bond vibration) through seconds, hours, or even longer, e.g., time for molecular diffusion and self-assembly. The size scales range from angstroms to nanometers to micrometers (e.g., length of the polymer to spatial extent of aggregates of molecules). The lattice models allow spatial coarse-graining of these features. In conjunction with MC methods, that enable various moves without reference to their hierarchy of relaxation time, many states can be generated rapidly and analyzed.

In the lattice MC method of polymers or surfactants, a chain molecule is first grown on either a two-dimensional or a three-dimensional lattice. The lattice polymer models achieve coarse graining of the physical space by employing a grid, and also coarse graining of polymer molecules by using united atom models. The chemical groups (e.g.,
alkane (CH$_2$/CH$_3$) groups) in the polymers are then represented as vertices of the grids in the lattice. The generation of an initial random configuration of a system consists of a random selection of a grid site, and a chemical group is then placed on this site. The next bonded group in the polymer chain is placed on a randomly chosen nearest-neighbor lattice site. This process is repeated until the entire chain has been grown.

In lattice MC simulations, the potential energy of a system in a given configuration is calculated by assigning interaction energy values to the pairs of atoms in the system. Consider, for example, a lattice occupied by atoms of type A and type B only and interacting via only nearest neighbor potentials. Interaction energies $\varepsilon_{AA}$, $\varepsilon_{AB}$, and $\varepsilon_{BB}$ can be assigned to the pairs AA, AB, and BB respectively. The potential energy of the system can then be expressed as,

$$V = n_{AA}\varepsilon_{AA} + n_{AB}\varepsilon_{AB} + n_{BB}\varepsilon_{BB}$$

(2.5)

where $n_{AA}$, $n_{AB}$, and $n_{BB}$, are the number of nearest neighbor pairs of type AA, AB, and BB on the lattice, respectively.

### 2.1.3 Monte Carlo moves

New configurations in MC simulations of lattice chain molecules are generated by four types of Monte-Carlo moves, namely, forward and backward reptation [73], chain translation, flip [74], and global cluster moves [49]. These moves represent different timescale motion of chains as explained below. Most of the simulation studies reported in the literature have employed only one or sometimes a combination of two of these
moves. The MC simulations carried out in this dissertation are unique in the sense that they have used all of these multi-timescale moves. A schematic representation of original configuration of a chain molecule on a square grid lattice, and its new configuration upon undergoing a reptation, flip, or global chain translation MC move is given in Fig. 2.2.

Figure 2.2 (a) original configuration of a lattice chain; configuration after, (b) reptation MC move, (c) flip MC move, (d) chain translation MC move.
In the reptation moves, an end group (head-group for forward reptation, and tail-group for backward reptation) of the surfactant chain is randomly selected. This is followed by a random selection of a nearest-neighbor site. The selected end group of the chain is then moved to this new site if it is vacant and the rest of the groups in the chain move in the same direction by one grid site or else the move is discarded. As the reptation move involves the motion of entire chain molecule, it is representative of a long-time scale move. In the flip move, a tail-group in a kink position is moved to an empty, diagonally opposite site on the square lattice. This is a small time-scale move, resulting only in a small change in the local conformation of the chain molecule. The random global translation of chain involves random selection of a group of a randomly selected chain and a random selection of a new grid site. The selected group is then moved to the new grid site while maintaining the original structure of the chain, provided all the new sites to be occupied by all the groups in the chain are empty. Global chain translation is a diffusion related move and has a very long relaxation time constant.

A global cluster translation move [49] is often used in the MC simulations of self-assembly of chain molecules in the solution. The initial dispersed solution of chain molecules (surfactants) achieves low-energy configuration by clustering into such structures as, spheres, cylinders, bilayers, etc. The sampling of phase space after formation of these clusters becomes very slow with the above described MC moves (reptation, flip, chain translation) and the system is vulnerable to getting trapped in a metastable state. To overcome this difficulty, a cluster move is generally employed in the
MC simulations of chain molecules. A cluster in the lattice MC simulations of surfactants is defined as a group of chains that have at least one group occupying nearest neighbor sites. The cluster move proceeds by first selecting, randomly, a group in a randomly selected chain. This is followed by a random selection of a new grid site. The selected group is then moved to the new grid site along with the cluster to which this chain is associated.

2.1.4 Configurational Bias Monte Carlo

Monte Carlo simulations of silane self-assembly on a substrate involve diffusion of chain molecules from the bulk solution to the substrate, and then relaxation of the deposited film. Standard Monte Carlo moves, such as, reptation, translation, cluster moves, and flip are very efficient for the diffusion of chains to the substrate. However, once the film has been formed, one end of the chain becomes fixed because of bonding to the substrate. Therefore, evolution of film structure with the standard MC moves becomes very inefficient, as these moves (with the exception of flip move) require collective motion of the entire molecule. Clearly, generation of new configurations and sampling of phase space becomes very inefficient with the standard MC moves in the simulations of self-assembled monolayers. This problem can be addressed by a method introduced by Siepmann et al [75] for simulations of dense polymer systems, known as configurational-bias Monte Carlo (CBMC). In this method, new configurations of a chain molecule are generated by completely reassembling the chain molecule or a part thereof.
The starting point for CBMC is a method first introduced by Rosenbluth and Rosenbluth [76] for the generation of configurations of polymers on a lattice. These authors employed a self-avoiding random walk for generating polymer configurations on a lattice, in contrast to the so-called “blind” random walk employed by conventional MC. The self-avoiding walk method came into being because of the inefficiency of the “blind” random walks in the sampling of phase space in lattice polymer systems. This point is described further in the following paragraphs.

In lattice MC simulations, the generation of a configuration of a chain molecule is a step-by-step process. A chain molecule comprising of ‘l’ segments is represented as connected grid sites on a lattice. First, a lattice site is selected at random for the placement of the first segment in the chain. Next, a nearest-neighbor site of the current polymer segment is selected at random for placing the next segment on the lattice. This procedure is repeated until the entire length of the chain has been grown. During this chain growth, the chains are not allowed to double back or cross themselves because of the constraints imposed by excluded volume; simply stated, no two polymer segments can occupy the same site at the same time. Therefore, in a lattice of coordination number ‘z’, the maximum number of possible sites for the placement of a chain segment is (z-1). In conventional MC, if a site selected during the chain growth is already occupied then the current attempt to grow the chain is discarded and a new attempt is made afresh. An example is illustrated in Fig. 2.3 (a) for growing a polymer chain with five segments on a two dimensional lattice. The first four chain segments are shown in lightly filled circles.
and direction of chain growth is shown with the help of arrows. After the first four segments of the chain have been placed on the lattice, as shown in Fig. 2.3 (a), the “blind” random walk procedure can select a site from all the three nearest neighbor sites of the fourth segment. If the site selected happens to be the one occupied by the second chain segment (Fig. 2.3 a) then placement of the fifth group on this site will violate the excluded volume condition. Therefore, the conventional MC discards the current attempt to grow the chain and a new attempt is made afresh. Clearly, in dense systems a growing chain will encounter many such obstacles and, therefore, the fraction of successful attempts in generating a chain configuration will be frustratingly low.

Figure 2.3 An illustration of chain growth on a 2-dimensional lattice, (a) "blind" random walk in conventional MC, (b) self-avoiding walk in Rosenbluth-Rosenbluth method.

The self-avoiding walk method of Rosenbluth and Rosenbluth addresses this inefficiency of the “blind” random walk by selecting a site for the chain growth only among those that are unoccupied. An attempt to grow a chain in self-avoiding walk method is discarded only when all the possible sites for placement of a segment are
occupied. This is illustrated in Fig. 2.3 (b); in contrast to the “blind” random walk that selected from all the three nearest neighbor sites of segment four, the self-avoiding walk selects a site from the two empty sites shown in dark filled circles. Therefore, self-avoiding walks result in a larger number of successful attempts.

However, because of excluded volume conditions, the configurations in self-avoiding walks are not generated with equal probability. This is illustrated in Fig. 2.4.
Figure 2.4 Possible configurations of a chain molecule with five segments in two dimensions.

Figure 2.4 represents possible configurations of a chain molecule with five segments in two dimensions such that the second segment is always to the right of the first segment. The first chain segment is shown with a dark filled circle and is connected to the segment with an arrow. The unfilled circles represent the positions of the second, third, and fourth segments in each chain configuration. The lightly filled circles represent the fifth segment of the chain and the numbers next to it represent the configuration taken.
by the chain molecule when the fifth segment is placed at that position. As can be seen in Fig. 2.4, the end group in the chain molecule can occupy any of the three possible sites in the configurations shown in the group A. In contrast, excluded volume conditions allow only two positions for the end group in the configurations shown in group B. Therefore, the probability of generating one of the configurations in group B is only 2/3, as against a probability of 1 for generation of configurations in group A.

Therefore, to count these configurations equally while taking the averages of a system property Rosenbluth and Rosenbluth introduced a weighting factor (Rosenbluth weight) for these configurations. The weighting factor is calculated at each step of the chain growth as follows,

\[ w_m = \frac{n'}{n} w_{m-1} \quad (2.6) \]

where \( n' \) is the number of available sites, \( n \) is the number of all possible sites, \( w_m \) is the Rosenbluth weight of the current segment, and \( w_{m-1} \) is the Rosenbluth weight of the previous chain segment (\( w_0 = 1 \)). The Rosenbluth weight of the completely grown chain is calculated as,

\[ W = \prod_{k=0}^{k=n'} w_k \quad (2.7) \]
where \( l \) is the number of segments in the chain molecules.

The CBMC method of Siepmann et al [75] extends the Rosenbluth-Rosenbluth (RR) method by taking into account the intermolecular interactions between the growing chain segments and its lattice neighbors. The empty neighbor sites for the growing chain in CBMC method are then selected based on their Boltzmann weight (in contrast to the random selection of the empty sites in the RR method). The Boltzmann weight of a site is given by,

\[
B_m(q) = \exp(-\beta \cdot u_m(q))
\]  

(2.8)

where \( m \) is the index of the growing chain segment, \( q \) is the index of one of the available sites for chain growth, and \( u_m(q) \) is the energy of segment \( m \) on site \( q \).

Specifically, for a lattice with coordination \( k \), the CBMC procedure selects a site for the chain growth with a probability,

\[
P_m(q) = \frac{B_m(q)}{\sum_{q=1}^{k} B_m(q)}
\]

(2.9)

A biased roulette wheel algorithm can be used for the practical implementation of selection of a site with the probability given by equation (2.9) [77]. In this algorithm, the interval between \( \{0, 1\} \) is divided in segments (Fig. 2.5) each with a size proportional to the probabilities \( P_m(q) \). A random number \( r \) is then drawn in interval \( \{0, 1\} \). A site is
chosen in whose segment number ‘r’ falls. Of course, a random number would more often fall in segments with larger area (Fig. 2.5). This procedure, therefore, leads to the selection of sites that have higher Boltzmann weights.

Figure 2.5 An illustration of roulette wheel algorithm method for selection of sites in a configurational-bias MC.

Since, the sites in CBMC are selected based on the Boltzmann weight, it necessitates the calculation of Rosenbluth weight as follows

\[ w_j = \frac{B_j(q)}{\sum_{q=1}^{k} B_j(q) w_{j-1}} \]  \hspace{1cm} (2.10)

Finally, acceptance of the trial configuration is decided based on the ratio of the Rosenbluth weights of the new and old configurations,
Next, as in the standard Metropolis method [18], a random number \( r \) is drawn in interval \( \{0,1\} \). If number \( r \) is smaller than ratio of Rosenbluth weights \( R \) then the new configuration is accepted or else rejected. This selection procedure ensures that the chain configurations are generated with the correct Boltzmann distribution and allows the calculation of average properties as in equation (2.3).

### 2.2 Deterministic methods

#### 2.2.1 Microcanonical molecular dynamics

A molecular dynamics simulation consists of solving numerically the classical equations of motion of a set of interacting particles. The solution results in the trajectory of the system, that is, the temporal evolution of the positions and the momenta of all the particles. The physical description of the system is made via a Hamiltonian that is written as the sum of kinetic energy and potential energy functions. The kinetic energy is typically a sum of quadratic functions of the particles’ momenta. The potential energy is usually a function of the particles’ positions. A simple formulation for the Hamiltonian of a system of \( N \) interacting identical particles is given by:

\[
H(\{p\},\{r\}) = \sum_{i=1}^{N} \frac{p_i^2}{2m} + V(\{r\})
\]  

(2.12)
where \( \{p\} \) and \( \{r\} \) stand for the momenta and positions of the \( N \) particles in some cartesian coordinate system; i.e. \( \{p\} = \{p_1, p_2, \ldots, p_N\} \) and \( \{r\} = \{r_1, r_2, \ldots, r_N\} \). The function \( V \) may be derived from first principles or expressed in the form of semi-empirical or empirical functions; some illustrative examples of such functions are given in section 2.2.5. By a particle, one understands not only a physical object, such as atoms or molecules, but also a pseudo particle (coarse grained CH2/CH3 in alkyl chains) or any other non-physical object that may be needed as part of the physical description of the system studied. For instance, in order to achieve isothermal conditions artificial degrees of freedom may be added to a physical Hamiltonian (section 2.2.4). In the simplest form of MD, the trajectories conserve the Hamiltonian (energy) and the number of particles.

### 2.2.2 Periodic boundary conditions

Additional boundary conditions are often imposed on the simulated system. Depending on these conditions, the trajectories may conserve either volume or pressure/stress. Free boundary conditions allow the system of particles to expand freely and therefore achieve constant pressure/stress conditions. One of the simplest forms of MD simulations is conducted at constant energy, constant number of particles and uses fixed periodic boundary conditions (PBC) to maintain the volume constant. For this, PBCs are such that when one particle leaves the box from one edge, another one enters the box from the opposite edge (Fig. 2.6). When imposing periodic boundary conditions, the potential energy function \( V \) includes the position of the particles in the periodic
images of the simulation cell. The intent of PBC is to mimic the behavior of a bulk material with the simulation of a computationally tractable small system. The artificial periodicity reduces free-surface effects that are inherent to small systems. With PBC the local environment of particles at the edges of the simulation becomes bulk-like. PBC, however, imposes unrealistic correlations in the simulated system for distances exceeding one-half of the length of the shortest edge of the simulation cell.

![Figure 2.6 A schematic representation of periodic boundary conditions in 2D](image-url)
2.2.3 Integration methods

In order to solve the equations of motion numerically, time is discretized [78]. The finite but small integration time step is typically a small fraction of the time necessary for one atomic vibration, that is typically on the order of 1 femto-second. Numerous numerical methods are available for the temporal integration of the coupled equations of motion. Some methods such as the leap-frog approach [79] offer the advantages of simplicity and low memory requirement, but entail the drawback of small time step for accuracy. Other higher-order methods, such as the predictor-corrector method allow for larger time-steps but necessitate larger memory allocations as well. Issues that need to be addressed in the choice of a numerical time-integrator relate to the conservation of the total energy in a microcanonical ensemble MD.

All numerical methods assume that the positions and dynamical properties, such as, velocity, acceleration, etc., can be approximated as Taylor series expansions:

\[
R_0(t + \Delta t) = R_0(t) + \Delta t R_1(t) + \frac{\Delta t^2}{2} R_2(t) + \frac{\Delta t^3}{6} R_3(t) + \frac{\Delta t^4}{24} R_4(t) + \cdots
\]
\[
R_1(t + \Delta t) = R_1(t) + \Delta t R_2(t) + \frac{\Delta t^2}{2} R_3(t) + \frac{\Delta t^3}{6} R_4(t) + \cdots
\]
\[
R_2(t + \Delta t) = R_2(t) + \Delta t R_3(t) + \frac{\Delta t^2}{2} R_4(t)
\]
\[
R_3(t + \Delta t) = R_3(t) + \Delta t R_4(t) + \cdots
\]
Equation 2.13 represents, Taylor series expansions of positions ($R_0$), velocity ($R_1$), accelerations ($R_2$), and so on. Some numerical methods are based on the Taylor’s expansions of only one of the above quantities and some are based on a combination of two or more of the above quantities. Some of these numerical methods are discussed below.

The simplest finite-difference method that is widely used in molecular dynamics simulations is a third order Verlet method [69, 70, 79]. Verlet’s algorithm utilizes a combination of two Taylor series expansions in particle positions. First, a Taylor series for positions is expressed from time $t$ forward to time $t+\Delta t$:

$$R_0(t + \Delta t) = R_0(t) + \frac{dR_0(t)}{dt} \Delta t + \frac{1}{2} \frac{d^2 R_0(t)}{dt^2} \Delta t^2 + \frac{1}{6} \frac{d^3 R_0(t)}{dt^3} \Delta t^3 + O(\Delta t^4) \quad (2.14)$$

Then another Taylor series for positions is expressed from time backward to time $t-\Delta t$:

$$R_0(t - \Delta t) = R_0(t) - \frac{dR_0(t)}{dt} \Delta t + \frac{1}{2} \frac{d^2 R_0(t)}{dt^2} \Delta t^2 - \frac{1}{6} \frac{d^3 R_0(t)}{dt^3} \Delta t^3 + O(\Delta t^4) \quad (2.15)$$

The above two expansions can be added to give:

$$R_0(t + \Delta t) = 2R_0(t) - R_0(t - \Delta t) + \frac{d^2 R_0(t)}{dt^2} \Delta t^2 + O(\Delta t^4) \quad (2.16)$$
The estimate of positions from the above algorithm contains an error that is of the order of $\Delta t^4$. Also, it can be noted that the Verlet's algorithm does not require the knowledge of velocities in order to estimate the positions for the next time step. There are, however, several ways by which velocities can be determined after the positions have been calculated.

Leap-frog method mentioned earlier, is a variation of Verlet's algorithm. This algorithm uses Taylor series expansions in both positions and velocities. The velocities $R1(t + \Delta t/2)$ are evaluated first at half time steps from the knowledge of velocities at time $(t - \Delta t/2)$. The positions are then calculated from the velocities $R1(t + \Delta t/2)$ together with the positions at time $t$. Therefore, effectively, positions leap-frog over velocities to give their values at $\Delta t/2$ time step ahead, and then velocities leap over positions by $\Delta t/2$ time step ahead, and hence the name. The equations for the leap-frog method are given as:

\begin{align*}
R0(t + \Delta t) &= R0(t) + \Delta t R1(t + \frac{1}{2} \Delta t) \\
R1(t + \Delta t/2) &= R1(t - \Delta t/2) + \Delta t R2(t) 
\end{align*}

(2.17)

One of the disadvantages of the leap-frog method is that positions and velocities both are not known at the same time. Therefore, total energy of the system cannot be calculated as a function of time.
Most of the algorithms falling under the Verlet class are perfectly adequate for most applications, however, sometimes it is convenient to employ higher order algorithms, such as Gear predictor-corrector method. Such higher order algorithm allows larger time steps, although, as already mentioned, at the cost of higher storage. Predictor-Corrector methods make use of Taylor series expansion in positions, velocities and also at least one another higher order derivative of position. Predictor-Corrector methods have three basic steps:

1. Prediction of positions velocities, accelerations, and other higher order derivatives of positions for the next time step.

\[
\begin{align*}
R_0(t + \Delta t) &= R_0(t) + R_1(t)\Delta t + R_2(t)\frac{(\Delta t)^2}{2} + R_3(t)\frac{(\Delta t)^3}{6} + R_4(t)\frac{(\Delta t)^4}{24} \\
R_1(t + \Delta t) &= R_1(t) + R_2(t)\Delta t + R_3(t)\frac{(\Delta t)^2}{2} + R_4(t)\frac{(\Delta t)^3}{6} \\
R_2(t + \Delta t) &= R_2(t) + R_3(t)\Delta t + R_4(t)\frac{(\Delta t)^2}{2} \\
R_3(t + \Delta t) &= R_3(t) + R_4(t)\Delta t \\
R_4(t + \Delta t) &= R_4(t)
\end{align*}
\tag{2.18}
\]

2. Calculation of forces \((F)\) and accelerations \((R_2^c)\) of particles with mass \(m\) at the predicted positions.
\[ F(t + \Delta t) = -\frac{dV(r, t + \Delta t)}{dr} \]  \hspace{1cm} (2.19)

\[ R^2(t + \Delta t) = \frac{F}{m} \]

3. Finally, correction of positions, velocities, etc., by using the difference in predicted acceleration and that given by the force evaluated at the predicted positions.

\[
\begin{align*}
\Delta R_2 &= R^2(t + \Delta t) - R_2(t + \Delta t) \\
R^0(t + \Delta t) &= R_0(t + \Delta t) + C_0\Delta R_2(t + \Delta t) \\
R^1(t + \Delta t) &= R_1(t + \Delta t) + C_1\Delta R_2(t + \Delta t) \\
R^2(t + \Delta t) &= R_2(t + \Delta t) + C_2\Delta R_2(t + \Delta t) \\
R^3(t + \Delta t) &= R_3(t + \Delta t) + C_3\Delta R_2(t + \Delta t) \\
R^4(t + \Delta t) &= R_4(t + \Delta t) + C_4\Delta R_2(t + \Delta t)
\end{align*}
\]  \hspace{1cm} (2.20)

In the corrector step, \(C_0, C_1, C_2, C_3, \text{ and } C_4\) are the predictor-corrector coefficients determined by Gear to ensure the numerical stability of the algorithm. These coefficients depend on the order of algorithm as shown in the Table 2.

<table>
<thead>
<tr>
<th>Order of equations</th>
<th>(C_0)</th>
<th>(C_1)</th>
<th>(C_2)</th>
<th>(C_3)</th>
<th>(C_4)</th>
<th>(C_5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1/6</td>
<td>5/6</td>
<td>1</td>
<td>1/3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>19/120</td>
<td>3/4</td>
<td>1</td>
<td>1/2</td>
<td>1/12</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>3/20</td>
<td>251/160</td>
<td>1</td>
<td>11/18</td>
<td>1/6</td>
<td>1/60</td>
</tr>
</tbody>
</table>
2.2.4 Canonical ensemble molecular dynamics

As mentioned in chapter 1, one of the objectives of this work is to investigate, via MD simulation, the effect of sliding friction on the silane monolayers used as an anti-stiction coating on MEMS surfaces. In these simulations two silane-coated surfaces are slid past one another and properties are calculated as real-time averages. An important issue in these simulations is the regulation of temperature in the silane monolayers. The work done in sliding past the two silane-coated surfaces is ultimately converted into heat. This heat is dissipated in an experimental set up from the alkylsilane monolayers into the underlying substrates. Canonical ensemble MD provides a way for the regulation of temperature in the simulations of processes such as sliding friction of silane monolayers.

The goal of isothermal MD (i.e., MD in the canonical ensemble) is reductionist. That is, canonical ensemble MD attempts to couple the atomistic degrees of freedom of the system of interest to a thermostat represented by a small number of variables only. The total energy is conserved in the microcanonical ensemble MD. In contrast, in the canonical ensemble, the equipartition theorem establishes a relationship between the temperature of the system and its kinetic energy [16]. Therefore, the total energy of the system fluctuates in an isothermal MD while the kinetic energy becomes a constant of motion. Any isothermal scheme has to satisfy the requirement that a time averaged property computed along a trajectory from an isothermal MD must equal its canonical ensemble average.
Several thermostating schemes are available for maintaining the temperature of a system in a canonical MD simulation, namely, the Andersen thermostat [80], the momentum rescaling method [81], Hoover's constraint method [82], and the Nosé-Hoover thermostat [82, 83] and chain of thermostats [84]. The Nosé-Hoover thermostat generates proper canonical distribution under specific conditions [69]. Therefore, in the simulations of friction between silane monolayers (chapter 5) Nosé-Hoover method is used to maintain the temperature at its desired value. A description of this method is given next.

The Nosé-Hoover thermostat is based on the use of an extended Lagrangian [80]. A Lagrangian is defined as the kinetic energy minus the potential energy.

$$L(\{p\}, \{r\}) = \sum_{i=1}^{N} \frac{p_i^2}{2m} - V(\{r\})$$ \hspace{1cm} (2.21)

In addition to the particle's degrees of freedom, the extended Lagrangian in Nosé formulation contains additional (artificial) thermostat degrees of freedom [69],

$$L(\{p\}, \{r\}) = \sum \frac{p_i^2}{2m} - V(\{r\}) + \frac{Q}{2} s^2 - \frac{L}{\beta} \ln s$$ \hspace{1cm} (2.22)
where $Q$ is an effective "mass" associated to the thermostat degree of freedom $s$. The following Hamiltonian for the extended system is then obtained,

$$H(\{p\}, \{r\}) = \sum_{i=1}^{N} \frac{p_i^2}{2m_i} - V(\{r\}) + \frac{p_s^2}{2Q} + L \frac{\ln s}{\beta} \quad (2.23)$$

Hoover simplified Nosé equation by eliminating the variable $s$, and thereby for each component of the position and momentum vectors, the following set of dynamical equations defines the Nosé-Hoover dynamics:

$$r_i = \frac{p_i}{m}, \quad i \in [1, N],$$

$$p_i = F_i - p_i \frac{p_n}{Q}, \quad i \in [1, N],$$

$$p_n = \sum_{i} \frac{p_i^2}{m} - Nk_B T,$$

$$\eta = \frac{p_n}{Q}. \quad (2.24)$$

The dynamics of the thermostat degree of freedom $\eta(=d\ln s/dt)$ is driven by the imbalance between the actual kinetic energy and the desired kinetic energy (through the desired temperature).

2.2.5 Interatomic potentials
Atomistic computer simulation methods (MD and MC) require a description of the interparticle interactions in order to yield a microscopic model of the system. Accurate MD or MC results are contingent upon the degree of realism of the microscopic description. The information about interparticle interactions is contained in the potential energy function, $V$. For continuous potential functions, the force field acting on a given particle is simply equal to the negative of its gradient.

A vast collection of microscopic models has been developed over many years. Early microscopic models range from discontinuous interactions (such as in the hard sphere model or square well potential model) to pair-wise additive continuous interatomic potentials of the Lennard-Jones, Buckingham and other variant forms [85]. Pair potentials were also developed for ionic crystals [86] and metals [87]. Microscopic models beyond pair potentials have also been developed to describe more realistic systems [88]. Examples of early empirical many-body potentials for describing covalent bonds include the Stillinger-Weber potential for condensed phases of silicon [89], Rahman-Stillinger potential for water [90], and Tersoff's potential for carbon [91]. One particularly successful example of a Tersoffian potential for hydrocarbons is the reactive empirical bond-order potential developed by Brenner [92, 93]. This type of potential can describe chemical reactivity, that is, chemical processes that involve bond breaking and bond forming [94]. Molecular mechanics non-reactive potential functions for organic substance based on harmonic descriptions of covalent bond stretching and bending are also available [95]. Charge transfer plays an important role in covalent bonding, especially
near surfaces, interfaces and defects. Alavi et al. proposed a charge-transfer molecular dynamics that is conservative [96]. This model was applied to the study of silica containing bond-breaking ions.

The potential functions used in this work are molecular mechanics potentials and can be interpreted in terms of a relatively simple three component picture of intra and intermolecular forces within the system. These components include harmonic potential forms for bond stretching and bond bending, and another component describing the interaction between the non-bonded parts of the system. The functional form of the potential can be expressed as:

\[
V(r) = \sum_{\text{bonds}} \frac{k_i}{2} (l - l_0)^2 + \sum_{\text{angles}} \frac{k_i}{2} (\theta - \theta_0)^2 + V(\text{r}_{\text{non-bonded}})
\]  

The first two terms in the equation model interaction between the bonded atoms. The first term models interactions between two bonded atoms A and B as a harmonic potential (Fig. 2.7 a) that results in increased energy as the bond length deviates from the reference value \(l_0\). Similarly, the second term also is a harmonic potential for three bonded atoms A, B, and C making an angle \(\theta\) (Fig. 2.7 b). Deviations of angle \(\theta\) from the reference value \(\theta_0\) again result in increased energy. The term ‘reference bond length’ and ‘reference bond angle’ is used to describe \(l_0\) and \(\theta_0\) as these are the values assumed by the bond lengths and bond angles when contribution from all the other potentials is
zero. Equilibrium bond length and equilibrium refer to the values adopted in the minimum energy structure when all the other terms also contribute.

Figure 2.7 An illustration of (a) bond stretching, and (b) bond bending.

A chemical bond between the atoms is usually very strong and requires very high energy for bond breaking. This is reflected in the very high values for the force constants for bond stretching. Whereas bending the bonds doesn’t require much energy and hence the force constants for bond bending are usually small.

The non-bonded interactions in equation (2.28) are calculated as coulomb potential for charged atoms, and as a Lennard-Jones (LJ) potential for non-polar atoms. The interactions between non-polar atoms are considered to contain two contributions, an attractive contribution for atoms at large distances, and a repulsive contribution for atoms at very small distances. The attractive interactions, also known as dispersive interaction, are long range and vary as \( r^{-6} \). The repulsive interaction at very short separation
distances is understood in terms of Pauli’s exclusion principle. The LJ potential models dispersive and repulsive interactions effectively, and is expressed as:

\[
V_{\text{LJ}}(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right]
\]  

(2.30)

where \( m \) and \( n \) are constants, \( x = r / r_m \), and \( r_m \) is the separation corresponding to the minimum energy. The best known form of Lennard-Jones potential (Fig. 2.3) is the 12-6 LJ potential for \( n=12 \) and \( m=6 \), and is expressed as:

\[
V_{12-6}(r) = \varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right]
\]  

(2.29)
Figure 2.8 The Lennard Jones potential
3 SURFACTANTS IN SOLUTIONS: MODELING INTERACTION BETWEEN HEAD GROUPS FOR SURFACTANT SELF-ASSEMBLY

As mentioned in chapter 1, MC simulation of self-assembly of alkylsilanes requires an appropriate set of interaction parameters. Few MC simulations studies of alkylsilane are available in the literature. In contrast, as reviewed in section 1.2.2, numerous MC simulations of surfactant self-assembly in solutions and on surfaces have been reported. Surfactants are amphiphilic molecules consisting of a hydrophilic head group and a hydrophobic tail. Surfactants and alkylsilanes are structurally similar with regard to their tails; both have a hydrocarbon backbone. However, one notable difference between these long chain molecules is that the head groups in alkylsilane are reactive and undergo a polymerization reaction in an aqueous environment. Still, the similarity in the tail structure of alkylsilanes and surfactants provides enough motivation for building an interaction model for alkylsilanes based on an acceptable surfactant model. However, there are ambiguous and contradictory opinions in the published literature with regard to the modeling of interactions between the surfactant head groups. Therefore, before a model is built for alkylsilanes (based on a model for surfactant molecules), it is imperative that the issues regarding modeling of head group interactions in surfactants be understood and investigated carefully. In this chapter, the issues relating to the ambiguity in the modeling of surfactant head group interactions are introduced. Also, a systematic MC simulation study conducted to understand the effect of the nature of interactions between the head groups on the surfactant aggregation behavior is described in detail.
The MC simulations of surfactants to date have used short surfactant chains having a structure $H_xT_y$, where H and T represent the head and tail groups of the surfactant chains. The main driving force for surfactant aggregation in these prior studies originates from an unfavorable interaction between the hydrophobic tail groups of the surfactant chains and the solvent (water), and a favorable interaction between the hydrophilic head groups and the solvent (water). Some studies also model the interaction between the head groups as short-range nearest-neighbor repulsion. The repulsive interaction between the head groups of the surfactant chains is considered to be responsible for limiting the size of the micelle.

Owenson and Pratt [97] have shown that to achieve surfactant aggregation yielding finite size micelles in simulations, one needs to include long-range repulsive interaction between the head groups. The views of Owenson were refuted by Smit et al [98] in their molecular dynamics studies of surfactant systems in which they showed the self-assembly of surfactant chains without any long-range interactions between the head groups. The views of Smit et al are well supported by numerous other simulation studies that have reported surfactant self-assembly with only short-range repulsive interactions between the head-groups. However, there is a notable difference between the structure of surfactant chains used in the studies of Owenson and Pratt and the ones used in the work of Smit et al and others. Owenson and Pratt modeled the surfactant chains with only one
head-group, whereas in the model of Smit et al, the structure of surfactant chains is $H_xT_y$, with $x, y \geq 2$.

This chapter investigates these opposing views by performing MC simulations of various surfactant models. The chapter is organized as follows. First, section 3.1 describes in detail the 2-D models used in studying the effect of the number of head-groups and the nature of the interactions between these groups on the aggregation behavior. Simulation results are presented in section 3.2. The different models studied in this work are compared on the basis of the CMC values obtained from the simulations. Several definitions existing in the literature have been used to determine the CMC values in the models studied. Since different definitions of CMC lead to different CMC values (in any given model), the comparison between models is done only within a given CMC definition. This is followed by a discussion of results obtained from these two dimensional simulations in section 3.2. This discussion is based on the concepts of free energy of micellization and excluded volume theory. Finally, this chapter concludes with a brief summary of the findings of this work in section 3.4 including a discussion of dimensionality effects and temperature effects on the simulations of the investigated surfactant models.
3.1 Models and Methods

In this work, the surfactant molecules are modeled as chains of connected grid sites on a two-dimensional square lattice. Representing the head groups by \( H \) and tail groups by \( T \), surfactant chains having two different \( H_x T_y \) structures are modeled, one with \((x = 1, y = 12)\), and another with \((x = 7, y = 12)\). The empty grid sites are considered to be occupied by the water molecules and are represented by \( W \). To understand the effect of long-range and short-range hydrophilic interactions on the micellization behavior of surfactant molecules in an aqueous solution, four different models of surfactant types and head-group interactions are considered, namely, strong long-range (SLR), short-range (SR), long-range (LR), and long head group (LHG). Surfactant chains of type \( H_1 T_{12} \) are used in models LR, SR, and SLR and surfactant chains of type \( H_7 T_{12} \) are used in the LHG model. In SR and LHG models, the head groups of surfactants \( H_1 T_{12} \), and \( H_7 L_{12} \) interact via a short-range nearest neighbor type interaction. In the LR and SLR models, the head-groups of \( H_1 T_{12} \) type surfactants interact via a long-range Coulomb interaction with a cutoff distance of 30 grid units. As will be seen later in this chapter, a stronger interaction value is used for the head group repulsion in the SLR model than in the LR model. For convenience, the structures of surfactant chains and the nature of interactions between the head groups in the various models are summarized in Table 2.
Table 3.1 Summary of surfactant chain structures and nature of HH interactions in various models.

<table>
<thead>
<tr>
<th>Model</th>
<th>Number of head groups</th>
<th>Number of tail groups</th>
<th>Nature of head-head interactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>LR</td>
<td>1</td>
<td>12</td>
<td>Long-range (Coulomb)</td>
</tr>
<tr>
<td>LHG</td>
<td>7</td>
<td>12</td>
<td>Nearest neighbor short-range</td>
</tr>
<tr>
<td>SLR</td>
<td>1</td>
<td>12</td>
<td>Long-range (Coulomb), interaction strength 10 times stronger than in LR model</td>
</tr>
<tr>
<td>SR</td>
<td>1</td>
<td>12</td>
<td>Nearest neighbor short range</td>
</tr>
</tbody>
</table>

Surfactant aggregation in the aqueous solutions is widely understood to be an entropic effect [99]. The surfactant chains in water aggregate to avoid the decrease in water entropy due to structuring of water around the free surfactant molecules. However, numerous successful simulations of surfactant models have been performed that ignore the water structure [41-51, 100]. These models employ an unfavorable energetic interaction between the tail and water groups. This interaction is often interpreted as an effective result of the interplay between energy and entropy gain that drives aggregation. Therefore, in the MC simulations of surfactant models discussed in this chapter, the energy and entropy effects are buried into an effective positive interaction energy term $\varepsilon_{WT}$. Also, a negative interaction energy term $\varepsilon_{WH}$ is used in all the models for the solvophilic head-water interactions. The interaction between a head group of one chain and a tail group of another chain, $\varepsilon_{HH}$, is assumed to be unfavorable and that it increases the energy. The interaction between the head groups of surfactant molecules is modeled
as a repulsive interaction, $\varepsilon_{HH}$. The potential energy of the water/surfactant system is then calculated by the following expression,

$$V = \varepsilon_{WW} \cdot n_{WW} + \varepsilon_{WT} \cdot n_{WT} + \varepsilon_{WH} \cdot n_{WH} + \varepsilon_{TH} \cdot n_{TH} + \varepsilon_{TT} \cdot n_{TT} + \varepsilon_{HH} \cdot n_{HH}$$  \hspace{1cm} (3.1)$$

where $n_{WW}$, $n_{WT}$, $n_{WH}$, $n_{TT}$, and $n_{HH}$ are the total number of water-water ($WW$), water-tail ($WT$), water-head ($WH$), tail-tail ($TT$), and head-head ($HH$) nearest neighbor contacts in the solution, and $\varepsilon_{WW} = 0$, $\varepsilon_{WT} = 0.77k_B T$, $\varepsilon_{WH} = -4.44k_B T$, $\varepsilon_{TH} = 0.77k_B T$, $\varepsilon_{TT} = 0$, and $\varepsilon_{HH} = 0.44k_B T$ ($44.4k_B T$ in the SLR model) are the interaction energies of the respective contacts and $T$ is 300 K. The interaction energies are chosen empirically such that a micelle like behavior is obtained in the simulations of the model surfactants. The interaction energy used for a water-tail contact appears to be consistent with the free energy change in transferring a surfactant chain from an aqueous environment to an oil-like environment. According to Stokes and Evans [101], the free energy change in transferring a surfactant chain from an aqueous solution to an oil-like interior is 3.0 KJ/mole per CH$_2$ group. Assuming two water molecules per CH$_2$ group, as in the case of a 2-D square grid surfactant model, this translates to 0.015 eV that agrees well with the water-tail interaction strength ($\varepsilon_{WT}$) of 0.019 eV (at room temperature). The interaction between the head groups compares well with the interaction between two point charges separated by a distance of 3 angstroms in
an aqueous medium. In the LR and SLR models, a Coulomb term is added to the equation (3.1) to account for the long-range interaction between the head-groups and is given by,

\[ V_{\text{long-range}} = \sum_{\text{pairs}} \frac{\phi}{d_{HH}} \]  

(3.2)

where \( \phi = \varepsilon_{HH} \), and \( d_{HH} = \) distance between the head-groups for \( 1 < d_{HH} < \) cut-off distance (30 grid units).

These models have been simplified by considering no interaction between the water molecules and no interaction between the tail-groups of the surfactant molecules. Also, the interactions between the head and tail groups are assumed to be the same as the interaction between the water molecules and the hydrophobic tail groups of the surfactant chains.

MC simulations are run in the canonical ensemble following the Metropolis method. First, \( N_{ch} \) surfactant chains \( (H_x, T_y) \) are introduced randomly in a square grid lattice of size \( L \times L \). These surfactant chains occupy \( N_{ch} (x + y) \) grid sites on the lattice and water molecules are assumed to occupy the remaining \( ((L \times L) - N_{ch} (x + y)) \) empty grid sites. The potential energy of the system in the initial random configuration is calculated using equation (3.1). The surfactant chains are then allowed to make MC moves on the lattice as explained in the section 2.1.3. A move is always selected if it reduces the overall
energy of the system. If an MC move results in an increase in the overall energy then this move is either accepted or discarded depending upon a transition probability given by equation (2.4). Several millions (about 8-12 million) of MC moves are used in all the cases to obtain reliable statistical averages once thermal equilibration is achieved. To eliminate any finite grid-size effects, simulations are run in four different grid-sizes (64x64, 128x128, 192x192, 256x256). The energy per chain for each grid size is plotted (Fig. 3.1) as a function of the grid size at a given surfactant concentration. Following definition is used for determining surfactant concentration,

\[ X_{ch} = \frac{N_{ch}}{(L \times L) - N_{ch} \cdot (x + y) + N_{ch}} \]  

(3.3)

where \( X_{ch} \) is the concentration of surfactant chains, \( N_{ch} \) is the number of surfactant chains, \( L \) is the grid size, and \( x \) and \( y \) are the number of head and tail groups, respectively, in a surfactant chain. It must be noted that these simulations are performed in a two-dimensional grid and hence the concentrations may differ from the experimental concentration values. A plateau is seen in all the energy versus grid size plots for a grid size of 192x192. This indicates that a grid size of 192x192 meets the requirement of thermodynamic limit and, therefore, most of the results presented in this chapter are taken from a simulation cell of size 192x192.
Figure 3.1 Energy per chain as a function of grid size at different surfactant concentrations.
3.2 Results and Discussion

3.2.1 Simulation Results

The results obtained from the simulations in SLR, SR, LR, and LHG models represented as plots of (a) the concentration of monomers (non-aggregated surfactant chains) in a simulation cell vs. overall concentration of surfactant chains, (b) energy per chain in a simulation cell as a function of overall concentration of surfactant chains, and (c) cluster size distributions. Each of these plots provides important insights into the physics and chemistry of the aggregation behavior in the aqueous surfactant solution. Prior studies have shown that cluster size distributions and plots of concentration of single chains as a function of overall surfactant concentration could be used for the determination of micellar properties, such as, critical micelle concentration, and aggregation number, etc. In this study, the energy per chain in a simulation cell as a function of overall surfactant concentration is also used for the determination of micellar properties.

3.2.1.1 Monomer concentration as a function of overall surfactant concentration

Monomer concentration is obtained as a function of overall surfactant concentration from MC simulations of the LR, LHG, SLR, and SR models and is plotted in Figs. 3.2 through 3.5, respectively. Several definitions of critical micelle concentration (CMC), based on the plots of monomer concentration versus overall surfactant concentration,
have been proposed in the literature. Care et al [48] have defined CMC ($X_C$) as the concentration at which a line of unit slope passing through the origin intersects a straight line through the monomer concentration beyond the onset of micellization. Israelachvili [102] has defined the CMC as the overall surfactant concentration at which the concentration of surfactant chains in the aggregates is equal to the concentration of monomers. Talsania et al [50] have used Israelachvili’s definition of CMC to define CMC ($X_T$) as the concentration at which a curve representing single chain concentration as a function of overall surfactant concentration intersects a straight line from the origin with a slope of 0.5.

Figure 3.2 Concentration of monomers versus overall surfactant concentration in the LR model.
It can be seen from Figs 3.2 and 3.3 that the single chain concentration in the LR and LHG models first rises with the overall surfactant concentration and then decreases slightly. Similar results have been reported in literature for surfactant chains with more than one head-group in relatively shorter chains [46-48]. The observed decrease in the monomer concentration at higher overall concentrations is also in agreement with the simulation results and experimental observations reported in the literature [46-48]. Care et al have been successful in predicting a decrease in monomer concentration beyond the CMC by applying a correction for non-ideality in the chemical potentials of the surfactants in the solution and the micelles in the mass-action model of Moroi [103].

Figure 3.3 Concentration of monomers versus overall surfactant concentration in the LHG model.
In Fig. 3.4 for the SLR model, in which the head-groups of the surfactant chains interact with a very strong long-range Coulomb interaction, the concentration of monomers keeps on increasing with the overall concentration of surfactant chains. This indicates that the solution remains largely a dispersion of single chains and that the strong repulsion between the head-groups does not allow these surfactant chains to come together despite the non-favorable hydrophobic tail-water interactions.

Figure 3.4 Monomer concentration as a function of overall surfactant concentration in SLR model.
Figure 3.5 represents monomer concentration in the SR model as a function of overall surfactant concentration. In this case, the single chain concentration is seen to be changing very slowly and staying very low relative to the overall surfactant concentration. Even at overall concentrations as low as \( \sim 1 \times 10^{-3} \), the single chain concentration is less than \( 3 \times 10^{-4} \). This indicates the readiness with which surfactant chains form aggregates when only the short-range interactions are present between the head groups of surfactant chains \( H_1T_{12} \). These results also provide an indication that the critical micelle concentrations for SR model lies below, and for the SLR model, lies above the concentrations studied in this work. Stated otherwise, in SR model the \( X_{CMC} < 1 \times 10^{-3} \), and in SLR model \( X_{CMC} > 4 \times 10^{-3} \).
Figure 3.5 Concentration of monomers as a function of overall surfactant concentration in SR model.

3.2.1.2 Energy per surfactant chain as a function of overall surfactant concentration

In Figures 3.6 through 3.9, energy per surfactant chain is plotted as a function of overall surfactant concentrations for all the surfactant models investigated.
Figure 3.6 Energy per surfactant chain as a function of overall surfactant concentration in LR model.
Figure 3.7 Energy/surfactant chain as a function of overall surfactant concentration in the LHG model.

It is seen that the energy per chain curve in the case of LR (Fig. 3.6) and LHG (Fig 3.7) models shows a change in slope. This result is similar to the experimental observations in which a solution property shows a change in the slope with respect to the overall concentration around the CMC. The CMC is then taken as the intersection of two linearly extrapolated lines. Therefore, the plots in Figures 3.6 and 3.7 are used to determine CMC \( X_{cm} \) based on energy in the LR and LHG models. The CMCs in the two cases are obtained by the intersection points of the linear regression lines on the initial and final portions of the data points. The CMC values thus obtained are \( \sim 2 \times 10^{-3} \) in both LR and LHG models.
The energy per chain in the SLR model (Fig. 3.8) keeps on increasing with the overall concentration. This result is due to the overwhelming repulsive interaction between the head groups of the surfactant chains that increases with the increasing concentration. As the strong repulsive forces inhibit chains from coming closer, the increased tail-water contacts also increases the overall energy.
In the SR model, the energy per chain in the investigated concentration range studied shows a slow monotonous decrease with increasing concentration (Fig. 3.9). This is similar to the high concentration behavior of LR and LHG models, suggesting that the CMC for this surfactant model is lower than the concentrations studied.
3.2.1.3 CMC from Cluster Size Distributions

Figures 3.10, and 3.11 display the cluster size distributions for each of the cases studied (SLR, SR, LR, LHG) for a high surfactant concentration and a low surfactant concentration in the solution, respectively.

Figure 3.10 A representative cluster size distribution at a (low) concentration of 7.39 x 10^{-5} in LR, SLR, and LHG models. The inset shows cluster size distributions in SR model at a concentration of 2.02 x 10^{-3} in the SLR model (inset).

In the low concentration regime (Fig. 3.10), the cluster size distributions are seen to be monotonically decreasing in all models, except for the SR model. In the SR model a shoulder is seen to be forming at small aggregation numbers, indicating the tendency of
surfactant chains to form aggregates even at low concentrations. This indicates that the lowest concentration studied in the SR model is greater than CMC.

![Figure 3.11](image)

Figure 3.11 Representative cluster size distributions in LR and LHG models at a (high) concentration of $5.18 \times 10^3$ and at a concentration of $4.36 \times 10^3$ in SR and SLR models. The inset shows cluster size distributions in the SR model at large cluster sizes.

At higher concentrations, as shown in Fig. 3.11, the cluster size distribution is again a monotonically decreasing function in the case of SLR model, indicating a dispersion of surfactant chains in the aqueous solution. Inset in Fig. 3.11 shows the cluster size distributions for SR model at high aggregation numbers. It is seen that it has peaks at very high aggregation numbers close to the number of chains in the solution and a peak at monomers. This provides further confirmation that the surfactant chains are more likely to form increasingly larger aggregates in the absence of any size limiting interactions.
between the head-groups. For LR and LHG, the cluster distributions show a shoulder. This is indicative of the presence of a micellar phase in the solution.

A theoretical definition of CMC ($X_{RN}$) based on cluster size distributions has been proposed by Nagarajan and Ruckenstein [104]. According to this definition, CMC is the concentration at which a transition in the shape of the micelle size distribution occurs from a monotonically decreasing function to the one possessing a minimum and a maximum. These authors defined a critical concentration as the one at which the cluster size distribution has a horizontal inflection point. This critical point is then taken as the close lower bound of the CMC. Following the definition of Nagarajan, the predicted values of CMC from the cluster size distributions of LR and LHG surfactant models exceed the CMC values that are obtained from definitions of Care, Talsania, and energy/chain. Therefore, the CMC definition proposed by Nagarajan does not appear to be adapted to the systems used in this work. Although a horizontal inflection point appears at a very high concentration, a change in slope with micelle size distribution occurs at a much lower concentration. This low concentration is in agreement with the values of CMC obtained based on the definitions of energy/chain and monomer concentration. Therefore, a less restrictive definition of CMC based on micelle size distribution is proposed as follows; CMC is the concentration at which an inflection point (horizontal or non-horizontal) is first seen in the cluster size distributions. This definition may be well suited for the solutions with smaller aggregation numbers, such as the ones
studied in this work. Using this definition the CMCs are determined to be \( X''_{\text{RN}} = 0.002 \) in the LR model, and \( X''_{\text{RN}} = 0.002 \) in the LHG model.

The CMC values obtained from different CMC definitions in LR and LHG models are summarized in Table 3. It is noted that although the different definitions of CMC lead to different values in a given model, within each CMC definition the LR and LHG models appear to have similar properties.

Table 3.2 Summary of CMC values in LR and LHG models

<table>
<thead>
<tr>
<th>CMC Definition</th>
<th>CMC LR model ((10^{-3}))</th>
<th>CMC LHG model ((10^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( X_T )</td>
<td>1.2</td>
<td>0.85</td>
</tr>
<tr>
<td>( X_C )</td>
<td>0.8</td>
<td>0.9</td>
</tr>
<tr>
<td>( X_{en} )</td>
<td>( \sim 2.0 )</td>
<td>( \sim 1.9 )</td>
</tr>
<tr>
<td>( X''_{\text{RN}} )</td>
<td>2.0</td>
<td>2.0</td>
</tr>
</tbody>
</table>

There appears to be a good qualitative agreement between the CMC trends obtained from 2-D MC simulations of the model surfactants studied in this work and the CMCs obtained from experiments. For example, experiments have shown that the CMC of non-ionic surfactants increase with increasing number of head-groups [101]. Also, higher CMC values are observed in the ionic surfactants than in non-ionic surfactants [101]. Similarly, a higher CMC is predicted for the non-ionic surfactant in the LHG model.
than for the non-ionic surfactant in the SR model ($N_{HG} = 1$). Also, the CMC values predicted for ionic surfactants in the LR and SLR models are significantly larger than the CMC values predicted for non-ionic surfactants in the SR model. The agreement between the predicted CMC values of non-ionic LHG model and ionic LR model seems to be a little surprising at this point, but a careful analysis of these results shows that this is only a dimensionality effect of the investigated models. A framework for the discussion of this dimensionality effect evolves in the next section. Therefore, a complete discussion of the dimensionality effect is included in the conclusions section at the end of this chapter.

3.2.2 Discussion of MC results

In the simulation of all the surfactant models (LR, SR, LHG, and SLR) studied in this work a surfactant structure is chosen with 12 hydrophobic tail-groups. Therefore, the hydrophobic effect driving the surfactant tails to aggregate in aqueous environment is expected to be the same in all these models. The difference in aggregation behavior in the four models would then appear to be a result of the different repulsive interactions between the head-groups in these models. In the LR and SLR models head-head interactions are long-range (Coulomb) in nature and in the SR and LHG models these interactions are short range (purely steric). The effect of these long-range and short-range interactions between the head-groups on the surfactant aggregation behavior is discussed below.
It is well known that the aggregation of surfactant chains in the aqueous solutions results from a hydrophobic effect, i.e., an effective unfavorable interaction between the hydrophobic tail-groups of surfactant chains and the solvent (water) [99]. Also, the existence of an opposing force is understood to be the reason behind the finite micelle sizes observed in the experimental solutions. This repulsive force in micelles primarily comes from the head-groups. In the case of ionic-surfactants the electrostatic charge on the head-groups is considered to be a major factor in providing the necessary repulsive force. For non-ionic surfactants, however, the repulsion is presumed to be steric in origin [99]. The free energy of micellization can, therefore, be expressed as,

\[ \Delta F_{\text{mic}} = \Delta F_{\text{rep}} - T\Delta S \]  (3.4)

In equation (3.4) \( \Delta F_{\text{rep}} \) is an energetic contribution that results from the repulsions between the head-groups of the surfactants, and \( -T\Delta S \) is the entropic contribution that results from the ordering of water molecules around the hydrophobic tail-groups. In the present simulations, the entropic contribution \( (T\Delta S) \) has been modeled as an unfavorable interaction \( (e_{\text{rep}}) \) between the surfactant tail-groups and water molecules. The change in free energy due to repulsion between the head-groups, \( \Delta F_{\text{rep}} \), is composed of an energetic contribution and a steric contribution, and is given by,

\[ \Delta F_{\text{rep}} = \Delta E - T\Delta S_{\text{conf}} \]  (3.5)
The energetic term \( \Delta E \) arises from an electrostatic repulsion between the head groups and the steric contribution \( -T\Delta S_{\text{conf}} \) is a result of the change in configurational entropy of the hydrophilic head groups of surfactants in the micellar state versus the surfactants in the isolated state.

The equivalence of the results in the LR and LHG models can be explained by comparing the free energy of micellization in the two systems. As the surfactant chains \((H,T)\) in both the models have equal number of tail-groups \((y=12)\), the entropic contribution \( -T\Delta S \) to the free energy of micellization \( \Delta F_{\text{mic}} \) in these two models is expected to be of the same order. The free energy of micellization in the LR and LHG models can, therefore, be compared on the basis of \( \Delta F_{\text{rep}} \) only. Furthermore, since the surfactant chains in the LR model consist of only one head-group, the entropic contribution to the repulsion between the head-groups \(-T\Delta S_{\text{conf}}\) is zero. The quantity \( \Delta F_{\text{rep}} \) in the LR model can, therefore, be represented as,

\[
(\Delta F_{\text{rep}})^{LR} = \Delta E^{LR} = \sum_{i'p'air} \frac{\phi}{d_{i'p'air}}
\]  

(3.6)

where, the summation index 'ipair' is the count of head group pairs in a micelle. In the LHG model, the energetic term \( \Delta E \) in equation (3.5) is due to a short-range (nearest neighbor) interaction between the head groups that ceases for the head groups separated
by grid spacing greater than 1 grid unit. The energetic contribution from the head group repulsions in LHG model is, therefore, negligible compared to the entropic contribution. The change in free energy due to head group repulsion in the LHG model can, therefore, be expressed as,

$$\left(\Delta F_{\text{rep}}\right)^{\text{LHG}} = -T \cdot \Delta S_{\text{conf}} \quad (3.7)$$

To gain a quantitative understanding of equations (3.6) and (3.7), a simple case is considered with a pair of only two surfactant chains. From equation (3.6), \(\left(\Delta F_{\text{rep}}\right)^{LR}\) in this simple case will be given by,

$$\left(\Delta F_{\text{rep}}\right)^{LR} = \frac{\phi}{d} \quad (3.8)$$

For determining \(\left(\Delta F_{\text{rep}}\right)^{\text{LHG}}\) in the LHG model, it is necessary to know the change in configurational entropy of the head groups as a function of distance between these groups. Following Flory [105], \(\Delta S_{\text{conf}}\) can be calculated by constraining the first head-group of the surfactant chains at a distance \(d\), and allowing the rest of the head groups to explore all the possible configurations. For each distance \(d\), the change in entropy, \(\Delta S_{\text{conf}}\), can be obtained from the following expression,

$$\Delta S_{\text{conf}} = k_B \cdot \ln \frac{W_d}{W_0} \quad (3.9)$$
where \( W_d \) is the number of possible configurations of the head groups when the first head groups of the interacting surfactants are separated by a distance \( d \), and \( W_0 \) is the number of configurations when they are separated by infinitely large distances. Therefore, the change in free energy due to head group repulsion in LHG model is given by,

\[
(\Delta F_{rep})^{LHG} = -k_B \cdot T \cdot \ln \frac{W_d}{W_0}
\]  

The calculation of the steric interactions based on equation (3.10) can be illustrated as follows. First, consider an isolated chain molecule with three groups on a two-dimensional lattice. All possible configurations of such a molecule can be represented as shown in Fig. 3.12. The black circle represents the constrained first head group of the molecule. The gray circle represents position of the second group of the molecule. The dotted circle represents possible sites for the third group. Since, the head groups of surfactant chains cannot fall into the hydrophobic core of a micelle, the configurations of chain molecule are constructed with the condition that the head groups do not fall below the lattice position of the first head group. With this condition, as seen in Fig 3.12, an isolated chain molecule on a two-dimensional lattice can have 7 different configurations. If two such chain molecules are present in a 2-D lattice at infinite distance, then the total number of configurations of the system will be \( W_0 = 7 \times 7 = 49 \).
Figure 3.12 All possible configurations of an isolated chain molecule on a 2-D lattice.

If these two chain molecules are brought closer to each other, then the number of possible configurations will be dictated by the excluded volume condition. This is illustrated in Fig. 3.13 that shows all possible configurations when the constrained first groups of the two molecules occupy nearest neighbor sites. The constrained first head groups are again represented with dark circles. The gray circles represent the position of the second head group of first chain and the dark square represents the second head group of the second chain molecule. The dotted circles represent the position of the third head
groups of the first chain, and the dotted box represents all the possible positions for the third head group of the second chain. As seen from Fig. 3.13, this two-chain system now has only 20 possible configurations as against 49 possible configurations when the constrained groups are apart at infinite distances. The values of \( W_0 \) and \( W_{d=1} \) can now be inserted in equation (3.9) and (3.10) to calculate \( \Delta S_{\text{conf}} \), and \((\Delta F_{\text{rep}})^{\text{LHG}}\). Therefore, the change in configurational entropy for bringing two chain molecules consisting of three segments, from an infinite distance to \( d = 1 \) is given by,

\[
\Delta S_{\text{conf}} = k_B \ln \left( \frac{20}{49} \right) = -0.9k_B
\]

and the change in free energy is given by,

\[
(\Delta F_{\text{rep}}) = -k_B T \ln \left( \frac{59}{100} \right) = 0.9k_B T'
\]
Figure 3.13 Possible configurations of a two chain molecule system when the head groups of these molecules are nearest neighbor and configuration of one chain molecule is fixed.
Based on the above analysis, the steric interactions between the head groups of a pair of surfactant chains of type $H_{112}$, for $x \in [2, 10]$ is calculated on a 2-D lattice and compared with $(\Delta F_{rep})^{LR}$ for a single pair of ionic surfactants $H_{112}$ in the Fig. 3.14.

![Figure 3.14 Illustration of steric repulsive interaction between the surfactant head groups as a function of distance between the constrained first head groups of the pair of surfactant chains.](image)

It can be seen in Fig. 3.14 that as the number of head groups ($N_{HG}$) in the LHG model increases, $(\Delta F_{rep})_{LHG} / k_B T$ becomes increasingly long-range. Also, for a given distance $d$
between the constrained first head groups of the two chains \( \left( \Delta F_{rep} \right)^{LHG} / k_B T \) increases with \( N_{HG} \). For instance, the steric interaction between the head groups of surfactant chains in LHG model is not negligible to \( \left( \Delta F_{rep} \right)^{LR} \), e.g., at a distance \( d = 4 \) between the constrained head groups of surfactant chains in the LHG model, and the head groups of the surfactants in the LR model, \( \left( \Delta F_{rep} \right)^{LHG} \sim \left( 1/3 \right) \left( \Delta F_{rep} \right)^{LR} \).

The above discussion, based on a pair of surfactant chains, can be extended to an aggregate of surfactants by considering a micelle of aggregation number \( N_{ch} \). Here, an estimate is made for a lower bound of the number of head-groups \( (N_{HG}) \), leading to a behavioral equivalence between the LR and the LHG models. The quantity \( \left( \Delta F_{rep} \right)^{LR} \) as given by equation (3.6), scales as the number of pairs of charged head-groups \( N_{ch} (N_{ch} - 1)/2 \) in the micelle. The major contribution to \( \left( \Delta F_{rep} \right)^{LR} \), however, comes from the head-groups that are separated by a minimum distance, \( d_{\text{min}} \). Therefore, for the sake of simplicity, \( \left( \Delta F_{rep} \right)^{LR} \), can be expressed as,

\[
\left( \Delta F_{rep} \right)^{LR} = N_{ch} \cdot (N_{ch} - 1) \cdot \frac{\phi}{d_{\text{min}}} \tag{3.11}
\]

In the LHG model, the number of possible configurations \( W_0 \) scales as \( \left( N_{conf} \right)^{N_{ch}} \), where \( N_{conf} \) is the number of configurations of the head-groups when the constrained
head groups of the surfactant chains are at infinitely large distances. The number of head group configurations at smaller distances \((W_a)\) would be much smaller compared to \(W_0\).

For example, in the simplest case of a compact micelle, only a very few configurations would be allowed by excluded volume. Therefore, the free energy of repulsion \((\Delta F_{\text{rep}})^{LHG}\), for an aggregate of size \(N_{ch}\) in the LHG model can be given as,

\[
(\Delta F_{\text{rep}})^{LHG} = k_B \cdot T \cdot N_{ch} \cdot \ln(N_{\text{conf}})
\]  

(3.12)

If the aggregate size \(N_{ch}\) is known, then a number of head-groups needed in the surfactants of the LHG model can be estimated that would give rise to a steric repulsion in the surfactants of LHG model (equation 3.12) comparable to the long-range electrostatic repulsion (equations 3.11) in the surfactants of the LR model. In the simulations of LR and LHG models an aggregation number of \(~4\) is obtained. Assuming \(d_{\text{min}} = 2\) grid-spacings for the head-groups in the LR model, equations (3.11) and (3.12) give \(N_{\text{conf}} = 28\). From the excluded volume condition it is calculated that in surfactant chains \(H_xT_{12}\) \((x \in [2,8])\), the number of possible head-group configurations are \(N_{\text{conf}} = [3, 7, 19, 49, 131, 339, 939]\). It is seen that for \(N_{\text{conf}} = 28\) there should be a minimum of 4 head-groups in the surfactant chains. It should be noted that this approach used to estimate \(N_{\text{conf}}\) for equivalence between the long-range repulsion in LR and steric
repulsion in LHG models provides only a lower bound for $N_{HG}$. This result is in a reasonable agreement with the surfactant chains used in simulations of LHG model.

The above analysis, therefore, provides an understanding that in order to achieve a finite size micelle in computer simulations of surfactant chains it is required that an excluded volume be provided to the head-groups of the surfactants. This requirement can be met by means of either the long-range repulsive interactions between the head-groups of surfactants of $H_{i}T_{12}$, $y \geq 2$, or by a sufficiently strong steric repulsion provided by increasing the number of head-groups in the surfactants.

3.3 Conclusions

A two-dimensional Monte-Carlo simulation study of the aqueous solutions of surfactant molecules has been conducted in four different models, namely, strong long-range (SLR), short range (SR), long-range (LR), and long head-group (LHG). Surfactant chains of type $H_{i}T_{12}$ have been modeled in the SR, LR, and SLR models with short-range, long-range Coulomb, and strong long-range Coulomb interactions between the head-groups, respectively. In the LHG model, surfactant chains $H_{i}T_{12}$ have been modeled with a short-range repulsion between the head-groups. Simulations have been carried out in a canonical ensemble with five Monte-Carlo moves- reptation (forward and backward), chain translation, flip, and cluster translation. The cluster translation move
has been found to be extremely important in the exploration of phase space following the formation of micelles.

The simulations indicate that with only short-range repulsion between the head-groups (SR model), the surfactants aggregate at very low concentrations and with very high aggregation numbers. The results of SLR model show that surfactants with very strong long-range cumbic interactions between the head-groups would largely remain a dispersion of monomers even at very high concentrations. The results of the LR and the LHG models have been found to be of similar nature despite the differences in the modeling of the interactions between the head-groups.

The agreement between CMC values of a non-ionic surfactant predicted by the LHG model and that of an ionic surfactant predicted by the LR models seemed surprising at first. However, based on arguments presented in section 3.2.2 it can be shown to be an effect of dimensionality of the simulation models. A simple analysis of the LHG model shows that for a given number of head-groups, the steric interaction \( \Delta F_{\text{rep}} \) is weaker for a 3-D cubic lattice than for a two-dimensional square-lattice. For example, from equation (3.10), \( \Delta F_{\text{rep}} = 0.8k_B T \left( W_d / W_0 = 16 / 25 \right) \) for two surfactant chains in a 3-D cubic lattice with constrained head-groups separated by a distance of 1 grid unit, whereas \( \Delta F_{\text{rep}} \) in a 2-D square lattice is estimated to be \( \sim 4.4k_B T \left( W_d / W_0 = 4 / 9 \right) \). The long-range interactions (equation 3.8) remain unaffected by system dimensionality. Based on these
arguments, surfactants in a 3-D LHG model are expected to have a lower value of CMC than the surfactants in a 3-D LR model. This result is in agreement with the experimental observations.

Although MC simulations have not been conducted at different temperatures, it is possible to predict the effect of temperature on the aggregation behavior of surfactants from the arguments developed in section 3.2. In all the models (LR, LHG, SR, SLR), the interactions between the various groups have been described via energetic terms. In principle, these interactions arise from entropic effects such as those associated with structuring of water around the surfactant chains. However, these entropic effects are buried in the energy terms ($\varepsilon_{ij}$'s) in equation 3.1. In the surfactant models studied in this chapter, the interaction energy terms ($\varepsilon_{ij}$'s) do not have any explicit temperature dependence. Therefore, the aggregation behavior of the modeled surfactants does not get affected due to the entropic contributions resulting from the structuring of water. However, as described in section 3.2, the head-group configurational entropic effects do come into play in the case of LHG model. As shown in equation (3.10), the free energy ($\Delta F_{rep}$) of two surfactant chains in the LHG model is predominantly steric in nature (much larger than $\varepsilon_{hh}$) and is temperature dependent. A higher temperature would, therefore, result in a stronger steric repulsion between the head groups and hence a smaller aggregation number for non-ionic surfactants in the LHG model. In contrast, the long-range interaction between the head-groups of ionic-surfactants in the LR model (equation 3.6) is independent of temperature.
Finally, results obtained from MC simulations indicate that it is important to have an excluded volume of surface head groups in order to obtain micellar type aggregates. This excluded volume can be obtained by either having energetic repulsions (long-range Coulomb type interactions) between the head groups, e.g., in the modeling of ionic surfactants, or by steric (entropic) exclusion by increasing the number of head groups in the surfactant chain, which could possibly be the case in modeling a non-ionic surfactant.
4 SELF-ASSEMBLY OF CATIONIC AND NON-IONIC ALKYLSILANES ON A CHARGED SUBSTRATE

Aqueous chemistries have recently been shown to be successful in the deposition of hydrophobic monolayer films of non-ionic and cationic alkylsilanes on hydrophilic substrates [12-14]. The hydrophobic films of alkylsilanes have been extremely successful in addressing the problem of stiction in MEMS. The ability to deposit alkylsilane films from an aqueous medium is very important as it addresses the concerns regarding generation of organic wastes in the conventional methods of alkylsilane film deposition. The alkylsilane films deposited from aqueous solutions have been characterized by electrochemical impedance spectroscopy (EIS) [14]. It is found from EIS that the self-assembled films of cationic alkylsilane deposited on a polysilicon substrate are more porous than the films of non-ionic alkylsilane [14]. The ionic group of cationic alkylsilane is hypothesized to be responsible for higher porosity seen in these films. A molecular level study of the structure of these films is needed in order to understand the origin of structural characteristics observed in the experimental alkylsilane films. Such an investigation will allow an understanding of the effect of ionic groups on the structure of self-assembled monolayer films. The existing experimental methods are still limited in their scope to allow a detailed examination of material systems at the molecular level. In contrast, atomistic simulation methods are a reliable alternative to investigate the systems of size and time scales that are involved in the examination of self-assembled films of alkylsilanes on the polysilicon surfaces of MEMS.
In this chapter, a two-dimensional MC simulation study is presented that simulates the self-assembly of model non-ionic and cationic alkylsilanes on a hydrophilic substrate. The impact of the charged group in cationic alkylsilane on the overall structure of the self-assembled films is investigated. The films are considered to consist of layers, where each layer may have head and tail groups in alkylsilane and water groups. The cationic and non-ionic alkylsilane film structures are characterized by spatial pair correlations at each of these molecular layers in the deposited films. The MC simulations reveal long-range correlations for the film of cationic alkylsilanes. Based on these 2-D simulations, an average "most probable" structure of the non-ionic and cationic alkylsilane films is determined.

The chapter is organized as follows. In section 4.1, a description of the cationic and non-ionic alkylsilane models used in the present study is given. The results obtained from the simulations are described and discussed in section 4.2 using head and tail group distribution profiles as a function of distance from the surface and spatial pair correlations at each layer of the film. Finally, the chapter is concluded with a brief summary of the findings of this work in section 4.3.
4.1 Models and Methods

In this chapter, coarse-grained two-dimensional models are developed for the aqueous solutions of cationic and non-ionic alkylsilanes. The choice of 2-D models is based on the ease in modeling and ease in computations. These models are used for studying the structure of self-assembled monolayers of alkylsilanes on polysilicon surfaces using MC simulation method. Coarse-grained models greatly simplify the physical description of the system and prove very useful for rapid sampling of phase space. Such coarse-grained models have been used successfully in the pioneering MC simulations of surfactants by Larson [41-45], and in MD simulations by Smit [106, 107]. Recently, coarse-grained methods have also been used for membrane studies by Klein and co-workers [108] and Marrink and co-workers [109]. In the previous chapter, models for surfactant molecules have been presented to simulate the aggregation behavior of these model surfactants in aqueous solutions. Because of the structural similarity between alkylsilanes and surfactant molecules, alkylsilane models used in this chapter are based surfactant model of chapter 4. Also, necessary modifications are made because of the inherent differences in the nature of the head groups in alkylsilanes and surfactants (in contrast to surfactant molecules, alkylsilanes consist of a reactive head group leading to polymerization reactions). Interactions are also included between the surface sites and the chemical groups in the alkylsilane to allow self-assembly of modeled alkylsilanes on a solid substrate.
The cationic and non-ionic alkylsilane molecules are modeled as chains of connected grid sites on a 2-D square lattice. Each non-ionic alkylsilane chain consists of one hydrophilic head group and 12 hydrophobic tail groups. The cationic alkylsilanes consist of a hydrophilic head group (non-ionic), 11 hydrophobic tail groups and a cationic group. The cationic alkylsilane used in the experimental studies [13] contains a (-CH₂)n segment, known as spacer, between the hydrophilic head group and the cationic group. Given that the chemical groups in the spacer and the hydrophobic tail are the same (-CH₂), no distinction is made between them and both are referred to as the tail groups. Figs. 4.1 (a) and 4.1 (b) show a simple representation of non-ionic and cationic alkylsilane chains on a 2-D square grid lattice, respectively.

A one-dimensional model is used for the hydrophilic surface. The grid sites (x ∈ [1, L], y = L/2) represent the surface sites on the hydrophilic substrate in a simulation cell of size (L x L). Under the conditions of experiments [12, 14], the pH of the alkylsilane
solution is maintained at ~ 4. The result is a distribution of –OH and negatively charged O' terminated sites on the hydrophilic surface. The hydrophilic head groups of alkylsilane chemisorb at the –OH terminated surface sites whereas cationic groups electrostatically physisorb to the O' terminated sites. Generation of a realistic distribution of –OH, and O' terminated sites in the surface model would necessitate simulation of large system sizes imposing a computational load difficult to attain on the available computer platforms. Therefore, in the surface model used here all the surface sites are assumed to be –OH terminated and a mean field approximation is made for the surface charges by distributing them uniformly across the entire surface. The choice of mean field approximation for surface charges is similar to the Gouy-Chapman treatment of surface charges frequently employed in the studies of surfaces [110, 111]. All the surface sites are, therefore, capable of both chemisorbing the hydrophilic head groups and interacting electrostatically with the cationic groups. In a simulation box of size $(L \times L)$ containing $N$ chains of alkylsilane, alkylsilane molecules occupy $13 \times N$ lattice sites, and $L$ sites are occupied by the surface. The remaining $\{(L \times L) - (13 \times N) - L\}$ empty grid sites are considered to be the water sites.

The energy model consists of nearest neighbor short-range interactions between pairs of non-ionic groups and long-range coulomb interactions between the pairs of charged groups. Representing water by $W$, head-group by $H$, tail-group by $T$, and surface sites by $S$, following pair interactions are included, $\epsilon_{WT}, \epsilon_{WH}, \epsilon_{HT}, \epsilon_{HH}, \epsilon_{SH}, \epsilon_{ST}$. The interactions between a pair of cationic groups of two different chains, and between a cationic group in
alkylsilane and charged surface sites are described by following Coulomb type interaction,

$$U_{\text{long-range}} = \sum_{\text{pairs}} \phi / d$$  \hspace{1cm} (4.1)$$

where $\phi$ is the Coulomb interaction between two charged groups separated by a unit grid distance, and $d$ is the distance between the charged groups. As charged groups do not see each other across the surface, no long-range interaction is calculated between the charged groups across the surface.

Usually, the long-range Coulomb potentials are calculated using Ewald sums method. However, Ewald sums are known to be computationally very expensive for systems with two-dimensional periodicity. It has been shown that accuracy in the calculation of Coulomb potentials is not significantly sacrificed by employing a truncation at reasonably large distances [112-114]. Also, a truncated coulomb potential provides at least a two-fold enhancement in computational speed compared to the Ewald sums method [112, 113]. Therefore, the truncation method is elected for the calculation of long-range interactions. A cut-off distance of 30 grid units is used, which has also been used in the previous chapter in simulations of surfactants. The total energy of the system is, therefore, given by the following expression,

$$U = (\varepsilon_{WT} n_{WT} + \varepsilon_{WH} n_{WH} + \varepsilon_{TH} n_{TH} + \varepsilon_{HH} n_{HH} + \varepsilon_{SH} n_{SH} + \varepsilon_{ST} n_{ST}) + U_{\text{long-range}}$$ \hspace{1cm} (4.2)$$
where $\varepsilon_{WT}$, $\varepsilon_{WH}$, $\varepsilon_{TH}$, $\varepsilon_{SH}$, and $\varepsilon_{ST}$ are the interaction energy values between different pairs of chemical groups, and $n_{WT}$, $n_{WH}$, etc. are the number of pairs of water-tail, water-head group and so on. The values of interaction energies used in the simulations are given in Table 4.

Table 4.1 Summary of interaction energies (in $k_B T$ units for $T = 300$ K) for various pair interactions in the non-ionic and cationic alkylsilane models

<table>
<thead>
<tr>
<th>Model</th>
<th>$\varepsilon_{WW}$</th>
<th>$\varepsilon_{WH}$</th>
<th>$\varepsilon_{WT}$</th>
<th>$\varepsilon_{HH}$</th>
<th>$\varepsilon_{HT}$</th>
<th>$\varepsilon_{TT}$</th>
<th>$\varepsilon_{SH}$</th>
<th>$\varepsilon_{ST}$</th>
<th>$\varepsilon_{SI}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-ionic</td>
<td>0</td>
<td>-4.44</td>
<td>0.77</td>
<td>-15.0</td>
<td>0.77</td>
<td>0</td>
<td>-15.0</td>
<td>1.55</td>
<td>0</td>
</tr>
<tr>
<td>Silane</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cationic</td>
<td>0</td>
<td>-4.44</td>
<td>0.77</td>
<td>-15.0</td>
<td>0.77</td>
<td>5.33</td>
<td>-15.0</td>
<td>1.55</td>
<td>5.33</td>
</tr>
<tr>
<td>Silane</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The interaction energies $\varepsilon_{WT}$, $\varepsilon_{TH}$, and $\varepsilon_{WH}$ are taken from surfactant models of chapter 4. The reactive head groups in alkylsilanes are believed to cause polymerization in the aqueous environment. Therefore, a very strong short-range nearest neighbor attractive interaction, $\varepsilon_{HH}$, is assumed between the head groups. To mimic chemical bonding, a value for $\varepsilon_{HH}$ is chosen empirically as the smallest energy that leads to polymerization of non-ionic alkylsilane in the bulk solutions in the long time limit. In the MC simulations discussed here, polymerization is said to occur when the head groups of two alkylsilane chains are nearest neighbors. Commercial cationic alkylsilane solutions used for coating applications consist of alkylsilane chains with a cationic group along the alkylsilane
backbone and mobile counter ions. For simulating the system without explicitly including the counter ions in the solution, the negative charge of the counter ions and the positive charge on the cationic group in alkylsilane chains is lumped together in a single effective interaction energy term $\varepsilon_{\text{eff}}$ representing a screened interaction.

To reproduce the dispersed cationic alkylsilane solutions, as seen in experiments [12, 14], interaction energy ($\varepsilon_{\text{eff}} = 5.3 k_B T$) is chosen empirically such that it produces a dispersed bulk solution. To simulate the chemisorption of alkylsilane on the (-OH) terminated hydrophilic surface sites, the models employ the same strong nearest neighbor attractive interaction ($\varepsilon_{\text{SH}}$) between the alkylsilane head groups and the surface sites as the head-head interaction ($\varepsilon_{\text{HH}}$). The hydrophobic tail groups have a short range nearest neighbor repulsive interaction ($\varepsilon_{\text{ST}}$) with the surface sites. Finally, the interactions ($\varepsilon_{\text{II}}$) between the cationic groups of different chains are long range repulsive and the interactions ($\varepsilon_{\text{SI}}$) between the cationic groups and the charges on the surface sites are long range attractive. Interaction energy between the water molecules is considered to be zero. All the interactions are relative to water-water interaction. Therefore, the repulsive interactions, $\varepsilon_{\text{WT}}$, $\varepsilon_{\text{HT}}$, $\varepsilon_{\text{ST}}$, $\varepsilon_{\text{II}}$ are positive and attractive interactions $\varepsilon_{\text{WH}}$, $\varepsilon_{\text{HH}}$, $\varepsilon_{\text{SH}}$, $\varepsilon_{\text{SI}}$ are negative.

All the simulations are run in a constant ($N, V, T$) ensemble with periodic boundary conditions. First, $N_{ch}$ number of chains is introduced in the simulation cell. The energy
of the random configuration is calculated from equation (4.2). The alkylsilane chains are then allowed to make MC moves on the grid. Four types of MC moves have been used in the simulations; forward reptation, backward reptation, global chain translation, global cluster translation. A cluster is defined as a group of chain molecules sharing nearest neighbor sites. The move is always accepted if it results in a decrease in the overall energy of the system. If the move results in an increase in the energy then the new configuration is either accepted or rejected on the basis of a transition probability, given by \( \exp(-\Delta U/k_BT) \). Here, \( \Delta U = (U_{\text{new}} - U_{\text{old}}) \) is the difference between the overall energies of new and old configurations.

The evolution of deposited films was studied using the CBMC method discussed in chapter 2. The implementation of this method involves selection of an alkylsilane chain \( i \) and one of its groups \( j \) at random. Next, all the groups of the chain after \( j \) (or with equal probability before \( j \)) are discarded. New sites for the placement of these groups are selected according to the Boltzmann weights of the available sites, as described in chapter 2. Rosenbluth weight of the new configurations is calculated using equation (2.7) and the new configuration is accepted based on the transition probability given by equation (2.11). The CBMC method is particularly important after the adsorption of the chain molecules on the surface when it is not possible to explore the phase space any further with the other conventional MC moves. The simulations are run for 50-100 millions of MC steps following the thermal equilibration.
4.2 Results and Discussion

MC simulations are used to study the self-assembly of ionic and non-ionic alkylsilane chains on the hydrophilic surface and to examine the structure of the deposited films. Simulations are run for three different starting concentrations, specifically, \( N_{ch} = [120, 220, \text{ and } 300] \) in a simulation cell of size 128 \( \times \) 128. Because of the periodic boundary conditions, for the hydrophilic surface located at \( (x \in [1, 128], y = 64) \), a maximum of 256 alkylsilane chains can attach to the surface sites with their head groups located at \( (x \in [1, 128], y = 63) \) and at \( (x \in [1, 128], y = 65) \). Therefore, the chosen concentration range allows exploring the self-assembly of alkylsilanes both below and above the concentration needed for the complete surface coverage.

Two separate procedures are used for film formation depending on the ionicity of the alkylsilanes. Cationic alkylsilanes are known to remain polydispersed over long periods of time. Owing to the stability of the experimental cationic alkylsilane solutions and to simulate the long-time limit solution state, the cationic alkylsilane solutions are thermalized for 2-5 million MC steps starting from an initial random configuration. During thermalization, alkylsilane chains are inhibited from occupying the surface sites by employing highly repulsive, short-range interaction energies for HS, TS, and IS pairs. Because of the repulsive Coulomb interactions, the cationic alkylsilane solution remains polydispersed with the formation of only a few small non-polymerized aggregates. Since the solution remains essentially polydispersed prior to deposition, the film structure is insensitive to the thermalization. Following this, the interaction energies given in Table 4
are used for the self-assembly of the alkylsilane molecules on the hydrophilic surface. Under experimental conditions, some kinetic constraints exist on the formation of polymerized clusters of non-ionic alkylsilane. Therefore, non-ionic alkylsilane solution can remain polydispersed for a small period of time prior to film deposition. Equilibrium MC does not impose any kinetic constraints on the polymerization. Therefore, to avoid the effects of this unrealistic clustering/polymerization on the film structure, the non-ionic alkylsilanes are allowed to self-assemble on the surface without prior thermalization from an initial random, polydispersed configuration employing the interaction energies given in Table 4.1.

Following the self-assembly of ionic/non-ionic alkylsilane chains on the surface, 50-100 million MC steps are used for the relaxation of the deposited films. After the relaxation of the deposited films, the following structural features are observed (a) alkylsilane chains with the head groups attached to the surface sites, (b) polymerized alkylsilane chains (i.e., a collection of alkylsilane chains in which head groups of chains share nearest neighbor sites), with the head group of at least one chain in the polymer attached to a surface site, and (c) chains in which head group is neither attached to a surface sites nor polymerized with a chain that has its head groups attached to a surface site. The first two types of alkylsilanes are referred to as the chemisorbed and the last type is referred to as the physisorbed. In actual experiments, the physisorbed alkylsilane chains are removed easily from the deposited films in the rinsing operations following film deposition. To simulate the rinsing of the deposited films the physisorbed alkylsilane
chains are identified and removed from the simulation box. The number of chemisorbed alkylsilane chains remaining on the surface (following the removal of physisorbed chains) in systems of different initial concentrations is given in Table 4.2. It can be seen that in rinsed systems the initial concentration has little impact on the concentration of chemisorbed alkylsilane. This indicates that even at the lowest concentration used in the simulations, the surface is saturated with the alkylsilane molecules. Following rinsing, the films of ionic and non-ionic alkylsilane are relaxed for 10-50 million MC steps and the structure of the relaxed films is investigated.

Table 4.2 Number concentration of alkylsilane chains on the surface before and after rinsing.

<table>
<thead>
<tr>
<th>Starting number concentrations of Non-ionic and Ionic silane chains</th>
<th>Number concentrations after Rinsing</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Non - ionic Silane</td>
</tr>
<tr>
<td>120</td>
<td>119</td>
</tr>
<tr>
<td>220</td>
<td>130</td>
</tr>
<tr>
<td>300</td>
<td>122</td>
</tr>
</tbody>
</table>

For illustration, Fig. 4.2 shows the snapshots of the films formed with non-ionic and cationic silanes on a hydrophilic surface in the 2-D MC simulations.
Figure 4.2 Snapshots of the (a) non-ionic, and (b) silane films following rinsing and relaxation.

The snapshots, such as the one shown in Fig. 4.2, are not sufficient to characterize unambiguously the structure of deposited films. Therefore, to gain a deeper understanding of the structure of the rinsed and relaxed films, following are calculated, (a) the head and tail groups distribution profiles perpendicular to the surface sites as a function of distance from the surface sites, and (b) spatial correlations of different pairs of groups along the surface. Figure 4.3 shows the tail group profiles as a function of distance from the surface. It is seen that a larger fraction of tail groups attach to the surface in case of cationic alkylsilane than in the case of non-ionic alkylsilane. These
results appear to be the effect of the ionic groups physisorbing to the surface sites. The hydrophilic head groups of alkylsilanes attach to the surface because of strong $(\epsilon_{SH})$ interaction, representative of the chemisorption of alkylsilane head groups on hydrophilic surface sites. The ionic groups attach to the surface sites due to the electrostatic interaction. The tail group (or spacer) between the head group and the ionic group in cationic alkylsilanes, therefore, occupies the surface sites due to the constraints imposed by the square grid lattice. Also, additional hydrophobic groups in the tail attach to the surface sites to screen the electrostatic repulsion between the cationic groups physisorbed on the surface. This leads to a high fraction of tail groups staying in proximity to the surface sites in cationic alkylsilane. This also results in fewer water groups attaching to the surface sites in the case of cationic alkylsilane.

![Figure 4.3 Tail group distribution profiles in non-ionic/cationic alkylsilane films as a function of distance from surface](image)

Figure 4.3 Tail group distribution profiles in non-ionic/cationic alkylsilane films as a function of distance from surface
From Fig. 4.3, it can also be seen that a higher fraction of tail groups is present in the layers of the cationic alkylsilane films closer to the surface. This indicates that the cationic alkylsilane films are more hydrophobic than non-ionic films. Experimentally, hydrophobicity is measured in terms of contact angles; higher contact angles representing more hydrophobic surfaces. The structure of the simulated films is therefore consistent with the higher contact angles (104±2° for cationic alkylsilane, 87±1° for non-ionic alkylsilane) observed in experiments for the cationic alkylsilane films [115]. Also, Fig. 4.3 shows that the non-ionic alkylsilane films have a higher thickness than the cationic alkylsilane films that is also consistent with the experimental observations [115]. Since, following rinsing only the chemisorbed alkylsilane chains remain in the system (with the head groups of most of these chains attached to the surface sites), distribution profiles for the head groups are not plotted. However, it must be mentioned here that only ~95% of head groups are attached to the surface sites in the case of ionic alkylsilane compared to 100% attachment in the case of non-ionic alkylsilane. Of course, this difference is due to the fact that fewer surface sites are available for head group attachment in case of ionic-alkylsilane in which ionic-groups and spacer groups also occupy surface sites. The head groups of remaining 5% chains are bonded to the head groups of the chains chemisorbed on the surface.

To obtain the correlations of different pairs of groups along the surface, the MC average number of pairs of AB (A, B = H, T, and W) is calculated, as a function of separation distance between A and B, on each layer of the film. The layers are numbered
from 0 for the layer occupied by the surface sites. Subsequently, these averages are converted to fractions following equation (4.3),

\[ R_{AB}^i(d) = \frac{\langle N_{AB}^i(d) \rangle}{\sum_B \langle N_{AB}^i(d) \rangle} \quad (4.3) \]

In the above equation, \( R_{AB}^i(d) \) represents the fraction of pair AB (e.g., \( A = H \), and \( B = W, AB = HW \)) on layer \( i \) when the distance between \( A \) and \( B \) is \( d \) grid units. The quantity \( \langle N_{AB}^i(d) \rangle \) represents the average number of pairs AB on layer \( i \) for a separation distance of \( d \), and \( \sum_B \langle N_{AB}^i(d) \rangle \) is the sum of all the AB pairs e.g. (\( A = H, B = H, T, W, \) and \( I \)) at separation \( d \) on layer \( i \).

For the illustration of this method two model structures are considered: (A) a layer with all the sites occupied by the head groups, and (B) a layer with periodically alternating clusters of head and tail groups, \( HH H H T T T T H H H H T T T T \ldots \), with a period of 8 grid units. Figs. 4.4 (a) and 4.4 (b) represent the calculated \( HH \) and \( HT \) correlations for the model structures (A) and (B), respectively. In Fig. 4.4 (a), as the % fraction of \( HH \) pairs at all the distances is 100, therefore, the probability of finding a head group at any distance from any other head group is 1.
Figure 4.4 (a) sample HH correlations for a layer completely occupied by head groups, (b) sample HH and HT correlations for a layer occupied by head and tail groups in an ordered form.

In contrast, in Fig. 4.4 (b) it is observed that the fractions of both $HH$ and $HT$ correlations at a distance of 1 grid unit are non-zero and fraction of $HH$ correlations is greater than $HT$ correlations. This indicates that there are more $HH$ pairs than the $HT$ pairs. Also, the positions of maxima in the $HH$ correlations indicate that the probability of finding a head group at a distance of 8, 16, 24 grid units from any other head groups is 1. This is consistent with the periodicity of the example structure used to calculate these correlations.
Arguments similar to those used above in explaining the example structures can be used to understand the more complicated structure of self-assembled films of alkylsilane obtained in the MC simulations. As already mentioned, three starting concentrations ($N_{ch} = 120$, 220, and 300) are used in these simulations. In this chapter, only the correlations obtained from systems with a starting concentrations of $N_{ch} = 220$ are discussed. Similar correlations are obtained for other concentrations.

Figs. 4.5 (a) and 4.5 (b) show the correlations for $HH$, $HT$, $HW$, and $HI$ on layer 1 for the non-ionic and ionic alkylsilanes, respectively. The following three observations are made from these plots (i) a much higher fraction of $HW$ pairs is seen on layer 1 for a non-ionic alkylsilane compared to the ionic-alkylsilane, (ii) much higher fractions of tail groups on the layer 1 in ionic alkylsilane, and (iii) the pseudo-periodicity of correlations for various paired groups in the ionic and non-ionic alkylsilane.
The observations (i) and (ii) above are consistent with the observations from the head and tail group profiles obtained perpendicular to the surface layer. The periodicity of correlations between different groups is used to construct an average picture of the film on the layer 1. Maxima are observed in the $HH$ correlations in ionic alkylsilane (Fig. 4.5 b) at distances of 1, 7, 15, 23 grid units and so on, indicating a high probability of finding a head group at these separation distances from any other head group. Similarly, maxima are also noticed in (a) $HI$ correlations at distances 3, 10, 18, (b) in $HT$ correlations at distances 5, 9, and (c) in $HW$ correlations at distances 4, 11 and so on. The positions of
the maxima in the plots in Fig. 4.5 (b), therefore, suggest the following average structure of ionic-alkylsilane on the layer 1:

\[ HHTIWHHTIWHHTI\ldots \]

The above structure indicates that the head groups are most likely to attach to the surface in the clusters of 2-3 head groups. The distance between the pairs of the head groups is 4-5 grid units. Also, the sharp peaks in the correlations indicate little variability in the arrangement of the \( H \), \( T \) and \( I \) groups on the surface.

For non-ionic alkylsilane, a higher fraction of \( HH \) correlations is observed at distances of 1 and 2 grid units. The maxima in \( HII \) correlations are observed at distances of 1, 8, 16, and 24 grid units with the loss of definite correlations at larger distances. Also, the fraction of \( HHH \) correlations stays larger than the \( HW \) and \( HT \) correlations at distances greater than 6 grid units. This suggests that the head groups in the non-ionic alkylsilane attach to the surface sites in clusters of 3-5 groups. The correlations in Fig. 4.5 (a) are not as sharp as in Fig. 4.5 (b). This indicates more variability in the size and spacing between the clusters of \( H \) and clusters of \( W \) groups along the surface. The \( HH \) clusters are separated by pockets of water of 4 to 6 grid units in size. Some occasional presence of tail groups is also indicated by the \( HT \) correlations that could be ascribed to the random high-energy events in the simulations allowed by the transition probabilities. From the
correlations of $HH$, and $HW$ the following structure of the non-ionic alkylsilane is predicted on layer 1.


For determining the structure of the film beyond layer 1, the $TW$, $TT$, and $TI$ correlations are looked at in layers 2 through to the top layer of the film. Fig. 4.6 shows these correlations for ionic alkylsilane. In rinsed films, there is no ionic group present beyond layer 3. Similarly, negligible number of head groups is present in the layers 2 and 3 that are thus ignored for the present analysis.

In Fig. 4.6 (a), oscillations in the $TT$ correlations are observed with a period of about 3-4 grid units. This suggests that the tail groups occupy the grid sites in layer 2 in clusters of 3-4 tail groups with these clusters separated by either an ionic group or a water group. The fraction of $TT$ correlations in layers 3-5 is much higher than the fractions of $TW$ and $TI$ correlations. Therefore, these layers are predominantly packed with the tail groups. Also, the fraction of $TW$ correlations in these layers, $R_{TW}^{3,4,5}(d)$, increases from $d = 1$ to $d = 3$ and then plateau. This indicates that the water groups are not dispersed and appear as a single cluster in this layer. Also, very low fraction of $TI$ correlations in layers 2 and 3 indicates that these layers are depleted of ionic groups, which is expected as most of the ionic groups are adsorbed on layer 1. The $TT$ and $TW$ correlations beyond layer 5 again
show a non-periodic structure. This structuring can be related to the presence of several clusters of tail groups separated by clusters of water groups.

Figure 4.6 TT, TW, and TI correlations in cationic alkylsilane on (a) layer 2, (b) layer 3, (c) layer 4, (d) layer 5, (e) layer 6, (f) layer 7, (g) layer 8, and (h) layer 9 of the film.

Also, it is observed that water groups become more predominant from layer 6 onwards. The presence of a single cluster of water groups in layers 2-4 and several clusters of water groups in layers 5 and 6 suggests that there could be at least one water filled pore in the film penetrating from the top surface of the film up to the layer 3 and several other pores of water penetrating up to layer 5. To help visualization of these water
pores, a schematic representation of the average deposited films with the water pores is shown in Figure 4.7. Also, presence of pores in the cationic alkylsilane film can be seen in the snapshot shown in Fig. 4.2. The fraction of $TT$ correlations, $R_{TT}^{i=7.8}(d)$, in Figs. 4.6 (g) and 4.6 (h) are seen to decrease from $d=1$ to $d=4$ with a still correlation at larger spacings. Therefore, the tail groups in these layers are expected to be present as cluster of 2-3 tail groups separated by water groups.

![Figure 4.7 A simplified representation of water pores in cationic alkylsilane film.](image)

Fig. 4.8 shows the $TT$ and $TW$ correlations in the non-ionic alkylsilanes. From Figs. 4.8 (a) through 4.8 (e), it is seen that the $TW$ correlations, $R_{TT}^{i=7.8}(d)$, increase from $d=1$ to $d=3$ and then plateau. Also, the fraction of $TT$ correlations is observed to be much higher than fraction of $TW$ correlations. Again, this indicates that these layers are mostly packed with the tail groups and water only appears as a single cluster of 3-4 water groups. In layers 6 through 9 progressively increasing levels of water are observed. There is an early indication of structuring of tail and water groups in layers 6 and 7 as the
correlations for these layers show a little peak between $d \in [30, 40]$. This peak is more pronounced in layers 7 and 8. The correlation distance in Fig. 4.8 (e) – 4.8 (h) suggests the presence of several clusters of the water groups separated by clusters of tail groups. Again, these correlations indicate that a water pore penetrates the film as deep as layer 2 and another water groove penetrates the film up to layer 5.

Figure 4.8 TT and TW correlations in non-ionic alkylsilane on (a) layer 2, (b) layer 3, (c) layer 4, (d) layer 5, (e) layer 6, (f) layer 7, (g) layer 8, and (h) layer 9 of the film.
A simplified representation of these pores is shown in Fig. 4.9. Also, looking at layers 8 and below, in the snapshot of non-ionic alkylsilane (Fig. 4.2 (b)), it is seen that fewer water filled pores are present in this film compared to the cationic alkylsilane film. Since there are fewer peaks in the layers 7 and 8 in non-ionic alkylsilane than in the case of ionic alkylsilane, it is predicted that the top surface of the deposited film is less rough in the non-ionic alkylsilane films than in the case of ionic alkylsilane. Finally, in layer 8 the switch between the water fraction and the alkylsilane fraction is complete. The shape of the two curves in layer 8 suggests that this layer is mostly occupied by water with very few tail groups.

Figure 4.9 A simplified representation of water pores in the non-ionic alkylsilane film.

4.3 Conclusions

The MC simulations in 2-D have been performed to investigate the effect of charged groups on the structure of non-ionic and ionic alkylsilane films deposited on a hydrophilic surface from aqueous solutions. The films of ionic and non-ionic alkylsilanes
deposited on a hydrophilic surface have been characterized by (i) calculating the
distribution profiles of the head and tail groups as a function of distance from the surface,
and (ii) spatial correlations between pairs of groups as a function of separation between
the groups along the surface. Both the distribution profiles and spatial correlations
indicate a higher porosity in the ionic alkylsilane films. Structures of simulated
alkylsilane films are consistent with the measurement of the contact angles of the as-
deposited uncured alkylsilane films [35]. Therefore, the equilibrium structures of non-
ionic and cationic alkylsilane films obtained from the simulations are expected to
represent the films that are obtained in the experiments prior to curing.

Simulations indicate that the morphology of the films is dictated by the topological
constraints on the alkylsilanes anchoring at the surface sites. In the 2-D simulations
cationic alkylsilane chains are seen to anchor at two surface sites with the chemisorption
of head groups and the physisorption of charged groups. Also, presence of cationic
groups is noticed in layers closer to the surface. A low energy configuration in the
cationic alkylsilane films is achieved by shielding of repulsive interactions between the
cationic groups by a higher density of tail groups in the lower layers. This topology of the
films in the lower layers also leads to higher porosity in the top layers of the cationic
alkylsilane films. It is expected that this higher density of hydrophobic groups near the
substrate is responsible for the higher contact angles seen for uncured cationic alkylsilane
films in experiments [8-9, 35]. In contrast, water pores have been observed in the layers
closer to the substrate in the case of non-ionic films.
Although, simulations have not been carried out to study the structures of the cured alkylsilane films, the nature of the cured films can be speculated based on the structures of the uncured films. Curing of the deposited films in experiments results in the removal of water trapped in the pores. Following the removal of water, the hydrophobic interaction, responsible for the folding of the hydrocarbon tail of alkylsilane in the aqueous environment, disappears. The hydrocarbon tails in the non-ionic alkylsilane can, therefore, stretch out resulting in films terminated by the terminal methyl groups in alkylsilanes. The methyl-terminated films have much higher contact angle than films that have methylene groups exposed.

As the MC simulations have been performed in two dimensions, no direct quantitative comparisons are made between the simulated and the real systems. Despite the limitations of 2-D systems in describing the real systems, important conclusions have been drawn from the structures of films obtained in the 2-D MC simulations that are strikingly consistent with the experimental observations. Very similar and more pronounced behavioral and structural features (porosity, etc.) are expected for the simulations of these systems in 3-D.
5 MOLECULAR DYNAMICS SIMULATION OF FRICTION BETWEEN ALKYLSILANE MONOLAYERS

The alkylsilane films have recently found applications in the fabrication of MEMS as they address the problem of stiction in these devices. However, in MEMS devices that have components with moving surfaces in contact, such as motors, gears, etc., friction between the moving surfaces becomes an important issue. The surfaces coated with a monolayer (or a few monolayers) thick alkylsilane films add another complexity in the study of tribological behavior of such surfaces. The tribological behavior of the alkylsilane films has become an important subject of study in the recent experimental and simulation investigations. Some of these studies have been reviewed in the section 1.1.3. The frictional behavior of the molecularly thin films in these studies is determined in terms of the friction coefficients of the deposited films as a function of separation between the probe and the coated surface, and also as a function of velocity of the moving surfaces. Simulations have also been used to investigate the frictional behavior of films under the environments of different hydrophobicities [116].

In this chapter, a simple model is developed to study the frictional behavior of the alkylsilane monolayer films deposited on a silica substrate. The model and the simulation method described here forms a building block for the next generation models to be used in the future studies of more complex phenomena occurring during the sliding friction of alkylsilane films, such as bond breaking and bond formation, effect of debris particles on the frictional behavior of the films and, friction between films under conditions of
varying humidity, etc. The MD simulations in this chapter are used to determine the frictional behavior of the model alkylsilane films as a function of separation between the films, the velocity of the moving substrates, and temperature. The chapter is organized as follows. In section 5.1 the structural models for the alkylsilane films and the silica substrates is presented along with the potential model used to simulate the dynamics of this system. The results from these MD simulations are presented and discussed in section 5.2. The chapter ends with the conclusions drawn from this study in section 5.3.

5.1 Model

The alkylsilane films on the practical MEMS structures are typically deposited on an amorphous silica substrate. However, in MD simulations it is convenient to model alkylsilane films bonded to a crystalline substrate while keeping the surface density of chain molecules similar to what is seen in the experimental films. In the current work, an α-cristobalite structure is used to model the silica substrate (Fig. 5.1.). The unit cell for this structure has dimensions of $4.97 \times 4.97 \times 6.92 \ \text{Å}^3$. The silica surface for monolayer deposition is constructed from an $(10 \times 10 \times 2)$ array of the unit cells of cristobalite, leading to surface dimensions of $49.7 \times 49.7 \ \text{Å}^2$ in the simulation cell. The silica substrate in this work is considered to be rigid, i.e., the real dynamics of the substrate atoms is not simulated. Therefore, effectively, this substrate structure serves the purpose of providing the sites for alkylsilane chain attachment and as a means to slide the films against each other.
The alkylsilane films in the experimental MEMS structures are chemisorbed to the Si atoms on the silica substrate via a Si-O-Si linkage (Fig. 5.2). Also, the head groups (Si(OH)₃) of the alkylsilane chains are known to crosslink, leading to a very rigid alkylsilane-substrate interface structure. Because of this rigid interface, it is convenient not to simulate the real dynamics of these (Si(OH)₃) head groups. Therefore, a simplified model is used with the hydrocarbon tail of alkylsilanes attached to the terminal Si groups on the cristobalite substrate. The united atom model is used to represent CH₂ and CH₃ groups as a single entity in the hydrophobic tail of the alkylsilane. Such coarse graining of the complex molecules is widely accepted in the MD simulations and describes the properties accurately when coupled with appropriate potential models. The structure of
the model substrate provides one site per unit cell for the alkylsilane chains. Therefore, the simulation cell consists of 100 alkylsilane chains on each substrate. This structure results in a density of 24.7 Å² per chain that is consistent with the density of alkylsilane films seen in experiments on amorphous silica substrates.

![Figure 5.2 A simplified representation of experimental alkylsilane films on a silica substrate.](image)

In the model developed here, the alkyl chains are attached to the terminal Si atoms on the α-cristobalite surface keeping the bond angles and bond lengths as specified in the Table 5.1. A mirror image of the bottom substrate and film is then used to generate the top substrate and film at a given distance from the bottom film. A schematic representation of the two alkylsilane coated α-cristobalite substrates is shown in Fig. (5.3). The substrates are made infinite in the X and Y directions by employing two-dimensional periodic boundary conditions. To simulate the friction between films, the top and bottom rigid substrates are set in motion at a constant velocity in the opposite
directions. The structure of alkylsilane films then evolves following Newton’s equations of motion.

Figure 5.3 A schematic representation of the initial structure of the alkylsilane films on \( \alpha \)-cristobalite substrates used in the friction simulations.

A molecular mechanics potential model is used to describe the interactions between different species in the simulation cell. The potential model includes intra-chain bond
strecthing and bond bending potentials, and also inter-chain and intra-chain 12-6 LJ potential. The intra-chain LJ potential is used for groups that are separated by three or more bonds. The interactions between the alkyl tails and the silica substrate are modeled as 12-6 LJ potential. The total potential energy of the system is given by the equation (2.28). The interaction parameters for the various potential terms are taken from a Universal Force Field (UFF) [117], and are summarized in the Table 5.1 below.

### Table 5.1 Parameters for harmonic bond stretching and bond bending potentials, and LJ interactions

<table>
<thead>
<tr>
<th>Bond length (Å)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂-CH₂</td>
<td>1.545</td>
</tr>
<tr>
<td>CH₂-CH₃</td>
<td>1.545</td>
</tr>
<tr>
<td>Si-CH₂</td>
<td>1.910</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bond Angle K(K/radian²)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂-CH₂-CH₃</td>
<td>62545.1</td>
</tr>
<tr>
<td>CH₂-CH₂-CH₂</td>
<td>62545.1</td>
</tr>
<tr>
<td>Si-CH₂-CH₂</td>
<td>96223.2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Lennard-Jones Parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Interaction Pair</td>
<td>σ (Å)</td>
</tr>
<tr>
<td>CH₂-CH₂</td>
<td>3.905</td>
</tr>
<tr>
<td>CH₂-CH₃</td>
<td>3.905</td>
</tr>
<tr>
<td>Si-CH₂</td>
<td>3.865</td>
</tr>
<tr>
<td>CH₃-CH₃</td>
<td>3.905</td>
</tr>
</tbody>
</table>
The frictional behavior of alkylsilane films in this work is characterized in terms of the friction coefficient of these films at different conditions. The friction coefficient in macroscopic experiments is defined as the ratio of the forces in the sliding direction $F_x$, and in the direction normal to sliding $F_z$, and is expressed as,

$$\mu = \frac{F_x}{F_z} \quad (5.1)$$

In the MD simulations performed here, the sliding and normal forces on the film are computed as the sum of the respective force components on atoms comprising a film and its corresponding substrate. The instantaneous force values are recorded during the course of the simulation, and the friction coefficients are determined as the ratio of the time average of the sliding force ($\langle F_x \rangle$) and normal force ($\langle F_z \rangle$),

$$\mu = \frac{\langle F_x \rangle}{\langle F_z \rangle} \quad (5.2)$$

The time averages of the sliding, and normal forces are computed by taking block averages of the force values, and the standard deviation of the average force values is calculated as the standard deviations of the block averages.
5.2 Results

In this section, the frictional behavior of the alkylsilane films deposited on a silica substrate is presented as a function of (a) the separation between the films, (b) the substrate velocity, and (c) the temperature of the films. The temperature of the films is maintained at the desired value by utilizing the Nose-Hoover equations of motion as described in the chapter 2. For the simulation of friction between the films, two alkysilane-coated substrates are slid against each other at constant velocity, temperature, and separation between the films. The flexible hydrocarbon tails of the alkylsilane molecules are very mobile and tilt during the sliding friction, making it difficult to define the separation between the films as the distance between the terminal CH₃ groups of the chains in the two films. Therefore, the separation between the films is defined as the distance \( D \) between the fixed (rigid) Si head groups of the films.

The results of friction simulations obtained in this work are described using a thermal activation model for friction due to Briscoe and Evans [118], which is introduced next. According to the thermal activation model, the plastic deformation in solids takes place by discrete processes involving a small number of molecules. The motion of a particular molecule during the deformation is restricted because of potential barriers due to the neighboring molecules. The height of these potential barriers increases by increasing the pressure (or normal force) and decreases by the application of a shear stress (or friction force). Representing the potential barrier as \( Q' \), the applied pressure as \( P \), and the shear stress as \( \tau \), the average time \( t' \) for a molecule to pass over the potential barrier can be
expressed as a product of a Boltzmann factor and the effective vibration frequency $f_0$ of the molecule,

$$\frac{1}{t'} = f_0 \exp\left\{-\frac{(Q' + P\Omega - \tau \phi)}{kT}\right\}$$  \hspace{1cm} (5.3)

where $-(Q' + P\Omega - \tau \phi)$ is the effective height of the potential barrier under the application of a normal load and shear stress. The factors $\Omega$, and $\phi$ are termed pressure activation volume, and the stress activation volume, respectively. The stress activation volume is interpreted as the size of the segment that moves in a unit shear process, and the stress activation volume is the change in local volume necessary to permit motion to occur.

Considering a regular series of such barriers separated by a distance $b$, and allowing transitions in both directions (forward and backward motion), the average velocity $\nu$ of the molecules down the potential gradient is given by,

$$\nu = 2f_0b \exp\left\{-\frac{(Q' + P\Omega)}{kT}\right\}\sinh\left(\frac{\tau \phi}{kT}\right)$$  \hspace{1cm} (5.4)

In a friction experiment, the sliding velocity $V$ of the substrate is considered to be proportional to the velocity of the rate controlling process $\nu$, allowing the equation (5.4) to be re-expressed as,

$$V = 2V_0 \exp\left\{-\frac{(Q' + P\Omega)}{kT}\right\}\sinh\left(\frac{\tau \phi}{kT}\right)$$  \hspace{1cm} (5.5)
where $V_0$ is an unknown velocity term. Equation (5.5) is treated as the basic equation in the thermal activation model of friction. In the work of Briscoe and Evans ($\tau \phi / kT > 1$), permitting equation (5.5) to be re-written as,

$$V = 2V_0 \exp \left\{ -\frac{(Q' + P\Omega - \tau \phi)}{kT} \right\}$$

(5.6)

The following functional relations between $P$, $\tau$, $T$, and $V$ are then derived from equation (5.6) considering that $P$, $T$, and $V$ are independent of each other,

$$\tau = \tau_0 + \alpha P$$

$$\alpha = \frac{\Omega}{\phi}, \tau_0 = \frac{1}{\phi} \left\{ kT \ln \left( \frac{V}{V_0} \right) + Q' \right\}$$

(5.7)

$$\tau = \tau_0' - \beta T$$

$$\beta = \frac{k}{\phi} \ln \left( \frac{V}{V_0} \right), \tau_0' = \frac{1}{\phi} \{Q' + P\Omega\}$$

(5.8)

$$\tau = \tau_0'' + \theta \ln V$$

$$\beta = \frac{kT}{\phi}, \tau_0'' = \frac{1}{\phi} \{Q' + P\Omega - kT \ln V_0\}$$

(5.9)

The results of the MD simulations of friction of alkylsilane monolayers are presented next, and are discussed in the context of equations (5.7), (5.8), and (5.9).
5.2.1 Compression of alkylsilane films

As described in the model section, to generate the initial configuration of the alkylsilane films the alkyl chains are anchored to the terminal Si groups of the α-cristobalite substrate with the length of the chain normal to the substrate. Before performing the sliding friction, this initial structure of the films is allowed to relax for 5 ps at zero substrate velocity. This is followed by a compression run at 2 Å/ps to obtain several configurations at different separation distances for use in the subsequent simulations of sliding friction.

The initial separation between the films during the relaxation run is set at 43.47 Å that corresponds to a separation of 12 Å between the terminal CH₃ groups of the chain molecules that are initially perpendicular to the substrates. This initial separation between the films is beyond the cut-off range of L-J interactions (~ 10 Å); therefore, there is no interaction between the films initially. Following relaxation, the films are seen to tilt from the normal direction, indicating that the natural structure of these alkylsilane films on the substrate is not perpendicular to the substrate.

Following relaxation, the upper alkylsilane coated substrate is moved downwards at the above stated compression rate. The configurations of the system are recorded every 500 compression steps (or every 1 Å) for use in the subsequent friction simulations. During the compression runs, the normal force on the films is recorded as a function of time. A plot of this data shows that the normal force on the film is zero for the first ~
9500 MD steps corresponding to separations ($D$) greater than 23.27 Å. The normal force on the alkylsilane films on the bottom substrate then increases to positive values, reaches a maximum, and then decreases to the negative values. A compression of 20 Å of these films would correspond to the overlap of 8 Å of films if the alkylsilane chains were to remain normal to the substrate. The minimum in the inter-film L-J potentials occurs at ~4.5 Å. The films should, therefore, experience a large repulsive force at these compressions if they were to remain perpendicular to the substrate. However, because of their flexibility, the films are able to accommodate these repulsive forces by tilting with respect to the surface normal. On further compression the films start interacting with each other. The nature of this interaction is attractive at first that becomes increasingly repulsive on increasing levels of compression. Also, in the plot of force versus displacement in Fig. 5.4, the compressive force (negative) on the bottom film is seen to oscillate at large compressions. As this plot is showing the instantaneous values of the normal load as a function of compression, it appears that these force values are not the steady state values and time scale for film relaxation is greater than the rate of compression.
Figure 5.4 Instantaneous normal force on the films during compression at a rate of 2 Å/ps as a function of MD time steps, one time step corresponds to 1 fs.

5.2.2 Sliding friction as a function of separation between the films

Following the compression of the films, MD simulations are performed for selected configurations, saved during the compression runs. The criterion for the selection of configurations is to choose those configurations that are under compressive force. The films on the bottom substrates are under compression when the net normal force on the film is negative. As mentioned earlier, the configurations obtained from the compression simulations are not the steady state configurations. Therefore, before starting the sliding friction simulations, the films are allowed to relax for 5 ps at the zero substrate velocity.
It is seen during this relaxation run that the normal force on the films relaxes to a lower value. The substrate velocity is then ramped up in the next 1000 MD steps to 1 Å/ps. Further relaxation of the normal force takes place during the substrate velocity ramp up and then the normal load acquires a steady state value in the next 1-2 ps. The force components in the sliding, and the normal direction are averaged for the next 10 ps. The friction coefficient for the sliding friction of the alkylsilane monolayers is calculated by taking the ratio of time average of the lateral force \( \langle F_s \rangle \) on the films to the time average of the normal force \( \langle F_n \rangle \). The average normal and lateral forces, and friction coefficients calculated for the various separation distances are given in Table 5.2. The data from Table 5.2 is used to plot friction force as a function of normal force, and also friction coefficient as a function of normal force. The friction coefficient in Fig. 5.5 is seen to decrease non-linearly with increasing normal force. This is in contrast to the definition of friction coefficient given in equation (5.2), which assumes a simple proportionality between friction force and the normal force. However, as seen in equation (5.7) from thermal activation model, the frictional force \( F_F = F_o + \alpha F_N \), therefore friction coefficient can be expressed as,

\[
\mu = \frac{F_F}{F_N} = \frac{F_o}{F_N} + \alpha \tag{5.10}
\]
The friction coefficient $\mu$ in equation (5.10) does show a non-linear relationship with normal force and data from the MD simulations is consistent with equation (5.7) of thermal activation model.

Table 5.2 Normal load, frictional force and friction coefficients as a function of separation between films

<table>
<thead>
<tr>
<th>Separation (Å)</th>
<th>Normal force (nN)</th>
<th>Shear force (nN)</th>
<th>Friction coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>24.47</td>
<td>-5.78 ± 0.18</td>
<td>-2.37 ± 0.10</td>
<td>0.39 ± 0.03</td>
</tr>
<tr>
<td>23.47</td>
<td>-9.32 ± 0.18</td>
<td>-2.83 ± 0.15</td>
<td>0.30 ± 0.02</td>
</tr>
<tr>
<td>22.47</td>
<td>-13.65 ± 0.17</td>
<td>-3.29 ± 0.22</td>
<td>0.24 ± 0.02</td>
</tr>
<tr>
<td>21.47</td>
<td>-18.96 ± 0.09</td>
<td>-3.79 ± 0.18</td>
<td>0.20 ± 0.01</td>
</tr>
<tr>
<td>20.47</td>
<td>-25.16 ± 0.22</td>
<td>-4.70 ± 0.31</td>
<td>0.19 ± 0.01</td>
</tr>
<tr>
<td>19.47</td>
<td>-29.94 ± 0.60</td>
<td>-5.75 ± 0.44</td>
<td>0.19 ± 0.02</td>
</tr>
</tbody>
</table>
Figure 5.5 Friction coefficient as a function of normal force.

Figure 5.6 Friction force as a function of normal force on the films.
In Fig. 5.6, the friction force is plotted as a function of normal force of the film. A linear fit to the data points is used to obtain the parameters $F_0$, and $\alpha$ as follows,

$$F_0 = 1.50 \pm 0.18 \text{ (nN)} \quad (5.11 \text{ a})$$

$$\alpha = 0.13 \pm 0.01 \quad (5.11 \text{ b})$$

5.2.3 Friction as a function of temperature

The frictional behavior of the alkylsilane films is examined as a function of temperature. The sliding friction simulations have been performed at the temperatures of 200, 300, 400, and 500 °K. The frictional force, the normal load and the frictional coefficient values at these temperatures are presented in the Table 5.3. A plot of friction coefficient as a function of temperature is shown in the Fig. 5.7.

Table 5.3 Normal load, friction force, and friction coefficient as a function of temperature.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Normal force (nN)</th>
<th>Shear force (nN)</th>
<th>Friction coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>-2.49</td>
<td>-2.23</td>
<td>0.90 ± 0.13</td>
</tr>
<tr>
<td>300</td>
<td>-5.78</td>
<td>-2.24</td>
<td>0.39 ± 0.03</td>
</tr>
<tr>
<td>400</td>
<td>-8.93</td>
<td>-2.54</td>
<td>0.28 ± 0.06</td>
</tr>
<tr>
<td>500</td>
<td>-11.50</td>
<td>-2.70</td>
<td>0.23 ± 0.06</td>
</tr>
</tbody>
</table>
Figure 5.7 Variation of friction coefficient as a function of temperature.

Figure 5.8 Friction force as a function of temperature.
From Fig. 5.7 it is seen that the friction coefficient decreases non-linearly with increasing temperature. The Friction coefficient is defined as a ratio of the frictional force and the normal force. Normally, in macroscopic solid surfaces the friction coefficient is a constant, implying that in order for sliding motion to occur, a larger frictional force would need to be applied at higher normal loads. However, for the sliding friction of alkylsilane monolayers examined in this work, it is seen from the data in the Table 5.3 that although the normal force on the films increases with increase in temperature, there is no appreciable change in the frictional force. This, therefore, results in a decrease in the frictional coefficient with increasing temperatures (Fig. 5.7). An explanation for this decrease in the friction coefficient is offered on the basis of the work of Glosli and McClelland [119]. According to these authors, the films on the substrates can be treated

Figure 5.9 Normal force on the films as a function of temperature.
as a collection of harmonic oscillators. At low temperatures, when the system is very weakly excited, the films behave harmonically. As the temperature is increased, the system becomes anharmonic. Thermal expansion results from anharmonicity of the potential in a confined space leading to increase in pressure or normal force. This anharmonicity of potential can also be related to the relative insensitivity of friction force to the increased normal force. As the system becomes anharmonic, the amplitude of vibrations increases and system can jump the surface potential barriers more easily.

By fitting their friction data to a thermal activation model proposed by Briscoe and Evans [118], Glosli and McClelland predict a linear relationship between the temperature and friction force. While these authors observe a drop in the frictional force at increasing temperatures, the frictional force in this work shows little variance as a function of temperature (a linear fit to the data in Fig.5.7 yields a slope of 0.0071 nN/K). This discrepancy appears to be the consequence of the assumption that the normal load in equation (5.8) is independent of temperature. The data obtained from simulations in the current work (Table 5.3) shows a clear dependence of the normal force (or load) on temperature. A linear fit to the data of normal force as a function of temperature gives the following relationship

\[ F_N(T) = -3.39874 + 0.0302047T \]

Inserting this temperature dependent load term in equation (5.7), and fitting the friction force versus temperature data to a linear function, the following parametric values are obtained,

\[ Q' / \phi = 9.24 \times 10^7 \text{ J/m}^3 \]

(5.12 a)
\[ \frac{k}{\phi} \ln \left( \frac{V}{V_0} \right) = -9.38 \times 10^4 \text{ J/(m}^3\text{K)} \quad (5.12 \text{b}) \]

The decrease in friction coefficient with increasing temperature is also consistent with the equation (5.8) after taking into account the temperature dependence of the pressure. Equation (5.9) can be re-expressed as

\[ \tau = \frac{1}{\phi} \left\{ Q' + P(T) \Omega \right\} - \beta T \]

Therefore, \[ \mu = \frac{\tau}{P(T)} = \frac{1}{\phi} \left\{ \frac{Q'}{P(T)} + \Omega \right\} - \beta T \cdot \frac{1}{P(T)} \quad (5.13) \]

From Fig. 5.9, it can be said that because \( P \) and \( T \) have a linear relationship, the last term in equation (5.13) is independent of temperature. However, because the first term is inversely proportional to the temperature, the friction coefficient will decrease with increasing temperatures.
5.2.4 Friction as a function of substrate velocity

The frictional behavior of the alkylsilane films is also investigated as a function of substrate velocity at 300 K for a separation of 24.47 Å between the films. The data for these simulations is presented in Table 5.4. In Fig. 5.10, the friction coefficient of the films is plotted as a function of substrate velocity, and in Fig. 5.12 friction force is plotted as a function of substrate velocity.

Table 5.4 Shear force, normal load, and friction coefficients as a function of substrate velocity.

<table>
<thead>
<tr>
<th>Velocity (Å/ps)</th>
<th>Normal Force(nN)</th>
<th>Shear Force (nN)</th>
<th>Friction coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>-5.78 ± 0.18</td>
<td>-2.37 ± 0.10</td>
<td>0.39 ± 0.03</td>
</tr>
<tr>
<td>1.5</td>
<td>-5.78 ± 0.09</td>
<td>-2.70 ± 0.04</td>
<td>0.47 ± 0.01</td>
</tr>
<tr>
<td>2.0</td>
<td>-5.94 ± 0.17</td>
<td>-2.99 ± 0.09</td>
<td>0.50 ± 0.03</td>
</tr>
<tr>
<td>2.5</td>
<td>-5.66 ± 0.19</td>
<td>-3.15 ± 0.16</td>
<td>0.56 ± 0.05</td>
</tr>
<tr>
<td>3.0</td>
<td>-5.76 ± 0.14</td>
<td>-3.22 ± 0.07</td>
<td>0.56 ± 0.03</td>
</tr>
<tr>
<td>3.5</td>
<td>-5.05 ± 0.13</td>
<td>-3.33 ± 0.06</td>
<td>0.66 ± 0.03</td>
</tr>
<tr>
<td>4.0</td>
<td>-4.83 ± 0.18</td>
<td>-3.35 ± 0.06</td>
<td>0.69 ± 0.04</td>
</tr>
</tbody>
</table>
Figure 5.10 Friction coefficient as a function of substrate velocity.

Figure 5.11 Normal load as a function of shear rate.
The data in Table 5.4 shows that the friction force increases with the increasing substrate velocity. This increase in the friction coefficient is a consequence of the increase in friction force with the increasing substrate velocity. The frictional behavior of the alkylsilane films as a function of substrate velocity is compared with equation (5.9) of thermal activation model. In contrast to equation (5.9), that predicts a linear relation between $\tau$, and $\ln V$, data obtained from simulations in the current work shows a non-linear relation between friction force, and $\ln V$ as seen in Fig. 5.12. Again, it is noted that in equation (5.9), the load $P$ is assumed to be independent of the substrate velocity, whereas data in Table 5.4 shows that the normal force (or load) is a function of substrate velocity. This modifies the equation (5.9) as follows,
The simulation data is fit to a linear function that relates normal force and the substrate velocity as, \( F_N(V) = 6.3396 - 0.319081V \). Inserting the substrate velocity dependence of normal force in equation (5.14) gives following parameter values,

\[ \tau = \left( \frac{Q'}{\phi} - \frac{kT}{\phi} \ln V_0 \right) + \frac{\Omega}{\phi} P(V) + \frac{kT}{\phi} \ln V \] \hspace{1cm} (5.14)

Solution of equations (5.11), (5.12), and (5.15) gives the following values of the various parameters: \( \phi = 140.54 \text{ Å}^3 \), \( \Omega = 18.73 \text{ Å}^3 \), \( V_0 = 3.37 \text{ m/s} \), and \( Q' = 7.83 \text{ KJ/mole} \).

The value of stress activation volume \( \phi \) is consistent with the periodicity of the lattice to which the alkylsilane head groups are attached, and the value of stress activation volume \( \tau \) is lower than the value of \( \phi \) which is consistent with the results of Brisco and Evans, as is the value of \( Q' \). However, the value of \( V_0 \) is inconsistent with equation (5.12b) that indicates a value of \( V_0 \) greater than the substrate velocity \( V = 100 \text{ m/s} \). This discrepancy appears to be due to the simple linear relationship assumed between \( F_N \) and \( V \).
5.3 Conclusions

The friction behavior of model alkylsilane films is investigated as a function of separation between the films, temperature, and the velocity of the substrate. The frictional behavior of these model films is found to follow the thermal activation model of Briscoe and Evans [118]. While the frictional behavior of the films in the experiments is examined as a function of load (normal force) on the film, the current work examines frictional behavior of the film at fixed separations between the films. One of the justifications for such an approach is that in the actual MEMS devices, e.g., gears, it is the separation between the alkylsilane-coated surfaces that is fixed. As a consequence, the normal force on the films in these simulations becomes a function of separation between the films, temperature, and the substrate velocity. Therefore, performing the simulations at a fixed distance between the films in this work allows the determination of the functional dependence of the normal force on temperature and velocity. Additionally, by taking into account this dependence of the normal force on these various parameters, the apparent discrepancy in the dependence of friction force on the temperature between this work and that of Glosli and McClelland [119] is successfully resolved.

The friction simulations in this work are performed at extreme conditions of velocity. The minimum substrate velocity used in this work is 1 Å/ps or 100 m/s. Although, this is an order of magnitude larger than the velocities used in friction experiments of alkylsilane films with AFM, the velocities used in this work are in the operating range of actual MEMS devices. The simulations of alkylsilane friction with the substrate velocity in the range of AFM probes would require much longer time and will be the focus of the
future work. However, it is notable that the results of the simulations are in agreement with the thermal activation model even at the extreme conditions of this work.
6 SUMMARY AND RECOMMENDATIONS FOR THE FUTURE WORK

In summary, this work has focused on the molecular simulations of self-assembly of surfactants in aqueous solutions, equilibrium structure of non-ionic and cationic alkylsilanes on a substrate, and friction between the alkylsilane monolayers on a silica substrate. These chemical systems form an important component in the fabrication of MEMS devices. The alkylsilane monolayers deposited on the MEMS surfaces render them hydrophobic and prevent stiction of surfaces during wet-etch release and during the operation of the device. Recent research efforts [10-14, 115, 120] have focused on the development of aqueous chemistries to minimize the organic waste resulting from the conventional methods of alkylsilane deposition on MEMS surfaces. These aqueous based chemistries utilize commercially available non-ionic and cationic alkylsilanes. The hydrophobic films obtained from the aqueous alkylsilane solutions have been found to be more porous for cationic silane films. The higher porosity of cationic alkylsilane films is hypothesized to be caused by the cationic groups. However, due to the limitations of the existing experimental methods, a molecular level picture of these films is still missing. In this work, a molecular simulation study is undertaken to investigate the equilibrium structures of cationic and a non-ionic alkylsilane films at the molecular level.

The MC simulation method has been chosen for simulating the self-assembly of alkylsilane on a substrate. The choice of MC method is based on the freedom of employing evolution processes with different time-scales to reach the equilibrium
condition. However, because of the lack of MC simulation studies of the alkylsilane systems in the literature, one of the tasks in this work has been the development of an appropriate interaction model for alkylsilanes. The structural similarity of the surfactant and alkylsilane molecules and the availability of a vast simulation literature on surfactant self-assembly are utilized in building an interaction model for alkylsilanes based on an acceptable surfactant model. The ambiguous opinions seen in the literature with regard to the modeling of interactions between the surfactant head groups have prompted, in this work, a detailed simulation study of surfactant systems. In the surfactant simulation literature, some researchers have favored the use of a short-range interaction between the head groups for the simulation of micellar type behavior, while others have preferred a long-range interaction. However, it was noticed that the proponents of short range interaction between the head groups utilized surfactant structures with more than one head group unit in their coarse grained surfactant model and the others used surfactant structures with only one head group unit. To understand these structural effects on the self-assembling behavior of the model surfactants, a detailed study of these systems has been undertaken in this work utilizing different surfactant models. The MC simulations show that the aqueous solutions of the surfactant chains with a larger head (larger number of head groups) and short range repulsions between the these head groups behave in a manner similar to that of the solutions of surfactant chains with only one head group that interact via a long range potential. These results are discussed on the basis of the free energy of micellization and are shown to be an effect of the similar excluded volume of head groups in the two interaction models.
Having developed the models for the surfactant self-assembly, the structural and interaction model for the alkylsilane have been developed with proper modifications for the head group interactions. This study involved simulation of self-assembly of model non-ionic and a cationic alkylsilane on a charged substrate. For the concentration range of alkylsilane examined in this work, the surfaces are seen to have become saturated with the chain molecules following a simulated rinsing operation. The structure of these relaxed films has been characterized by examining the tail-group profiles as a function of distance from the substrate and also the spatial correlations of various pairs of groups along the substrate. The tail group profiles have revealed that a larger number of tail groups occupy grid sites closer to the substrate in the case of cationic alkylsilane. This higher concentration of tail groups is predicted to be the effect of both the dimensionality of the simulated system and presence of tail groups between the charged groups to screen the repulsive interaction between these groups. The tail group profiles have also indicated a higher thickness for the non-ionic alkylsilane films in agreement with the experimental films.

The spatial correlations of the various pairs of groups along the substrate have also shown a larger fraction of tail groups residing closer to the substrate in the cationic alkylsilane films. The pair correlations also show the presence of water filled pockets in the layers closer to the substrate in the non-ionic silane films and a rougher top surface for the cationic alkylsilane films. These film structures have been found to be consistent with the measurements of contact angles of uncured experimental alkylsilane films. The
presence of water filled pockets near the substrate in the non-ionic alkylsilane films is predicted to be the cause of the lower contact angles seen in the experimental uncured films. Also, the roughness of the top surface of the cationic silane film in both the experiments and the simulations is believed to be the topological effect of the structure of the films in the lower layers.

One limitation of the MC simulations presented here is that the dimensionality of the simulated systems does not allow any direct comparisons of the simulation results with those obtained from the experimental studies. However, the qualitative behavior of the simulated systems has been found to be similar to the experimental systems in both the surfactant self-assembly in solutions and the alkylsilane self-assembly on surfaces. The effect of temperature on the surfactant self-assembly has been predicted qualitatively based on the free energy of micellization. A better quantitative understanding of these systems can be gained by performing these simulations in three dimensions. In the three-dimensional simulations a larger number of configurations would be available to the chain molecules for relaxation. The 3-D simulations could also be used as a tool to verify the arguments presented for the effect of temperature on the self-assembling behavior of the various surfactant models by performing a series of simulations at different temperatures.

Also, the behavior of the three-dimensional non-ionic and cationic alkylsilane systems is predicted based on the findings of this work. The MC simulations of the
alkylsilane self-assembly can also gain from three-dimensional simulation. However, these would be very expensive computationally. The 3-D simulations of alkylsilane monolayer self-assembly can benefit immensely from the use of a grand canonical ensemble as opposed to the canonical ensemble simulations used here. In the grand canonical ensemble simulations the number of chain molecules can be allowed to change keeping the volume, temperature, and chemical potential of the alkylsilanes constant. These simulations would be of interest as the self-assembly of alkylsilanes on the substrate can begin from a relatively dilute bulk solution preventing any bulk polymerization. Then as the alkylsilane chains diffuse to and adsorb on the substrate, the bulk solution can be replenished by insertion of new chains maintaining a constant chemical potential in the bulk.

Finally, MD simulations of friction between the alkylsilane films have been performed. The contribution of this work is a simple model that is capable of investigating the frictional behavior of these complex systems. Despite its simplicity and the extreme conditions of simulations, the model successfully predicts the frictional properties of the alkylsilane systems that are consistent with a thermal activation model due to Briscoe and Evans. The current work also makes a contribution to the model of Briscoe and Evans in that it clearly shows the dependence of the pressure on the films, on the temperature and the velocity of substrates.
The future studies of friction of alkylsilane monolayers can involve simulations of these films at different densities. For example, at very low densities the alkylsilane chains would be able to interpenetrate. In such a situation the entropy of the system might play a crucial role in determining the frictional properties of these films and will be worth examining. In the current work, the temperature of the film is maintained by coupling the degree of freedoms of the film atoms to a Nose-Hoover thermostat. However, in the real systems the heat generated during the friction of films flows to the substrate. The realization of such a process can be achieved by simulation of the real dynamics of the substrate atoms. The future simulations can model a silica substrate with a rigid layer of atoms topped by the thermostated layer of atoms. The rigid layer of substrate atoms can be used to give a constant velocity to the system for sliding friction, while the heat generated in the films during friction can be dissipated to the thermostated substrate atoms. One of the difficulties associated with the simulations of real dynamics of the silica substrate atoms is that most commonly used potential (BKS) for silica results in a surface that is oxygen rich. Therefore, any attempts to start the simulations of friction with the configurations of the substrate and alkylsilane films used in this work, would result in the collapse of the alkylsilane films into the substrate (as the terminal Si atoms on the silica surface get sucked into the substrate). This would require the development of appropriate interaction models for interactions between the substrate atoms and the alkylsilane atoms to impart the system needed stability. Another option could be to first generate a relaxed, oxygen terminated silica surface and then anchoring alkylsilane chains to the oxygen sites.
Friction studies can also involve development of all-atom models for the alkylsilane films and the use of a reactive bond order (REBO) potential. Such models can simulate the tribochemistry of the system, i.e., reactions between the species during friction. The REBO potentials have been used in the past in the simulation of friction between diamond surfaces terminated with small hydrocarbon molecules and predict the effect of bond-breaking and bond-forming on the overall friction behavior of these surfaces. No such study is currently available for the friction of alkylsilane films.
REFERENCES


