ABSTRACT

KING, MARIAH JAYNE. Theoretical Analysis of Interfacial Phenomena during Thin Film Growth and Surfactant Characterization. (Under the direction of Erik Santiso and Gregory Parsons.)

Computational resources offer an unprecedented opportunity to explore interfacial systems. A majority of research in the area of computational exploration and interfacial systems is sponsored by industrial concerns to efficiently develop novel processes, increase accuracy and environmental compatibility of large-scale processes. Engineers and scientists in an experimental setting are often responsible for exploring an outstanding number of variables involved in a chemical process, but are limited to a narrow scope of chemistries. Collaborations between experimentalists and computational scientists bridge this gap and allow for a more in-depth exploration of the system at hand. This collaboration is highly beneficial since it offers a more comprehensive understanding of interfacial systems. In this thesis, we demonstrate the use of first principle and coarse-grained molecular dynamics to further the understanding of interfacial behavior in the semiconductor and surfactant industry. Two projects focus on the nucleation of various precursors on two commonly used surfaces for atomic layer deposition of thin films for electronic device fabrication and the two projects focus on the behavior of surface acting agents (surfactants) at a water vapor-liquid interface and the method used to generate information for 100+ topologies.

In the first two projects, we present a detailed analysis using density functional theory to provide novel insight into mechanisms that govern nucleation during tungsten atomic layer deposition (W-ALD). We use calculated surface reaction energetics to suggest the most probable series of reactions that lead to monolayer formation during sequential doses
of WF$_6$ and SiH$_4$ on desired growth surfaces, silicon (Si(100)) and tungsten (W(110)). We show that for the initial nucleation of WF$_6$ on silicon, a relatively high-energy barrier exists and that for both half-reactions, release of H$_2$ is significantly favored over HF. In the second half-reaction, we show that SiH$_4$ plays a crucial role of saturating the deposited W layer with silicon hydrides. Overall, the calculated energetics, along with experimental evidence, allow us to propose the most probable by-products released during the ALD process. Additionally, we present energetics for nucleation reactions that occur during Area-Selective Atomic Layer Deposition of TiO$_2$ and W. We propose nucleation schemes that support native selectivity between substrates as well as pathways that lead to non-selective growth. The presented results reveal a novel approach for determining surface site selectivity during ALD processes for various precursor chemistries.

In the last two projects, we present results from coarse-grained molecular dynamics simulations illustrating the relationship between the tail group topology and alcohol ethoxylates (AE) and their ability to lower the surface tension at the water vapor-liquid interface. We find that branching of AE surfactants allows for a range of water vapor-liquid surface tension values ranging from 10 mJ/m$^2$ to 65 mJ/m$^2$. Our results indicate that branch location and head to tail bead ratio significantly impacts a surfactant’s ability to lower the surface tension at the vapor-liquid interface of water. Furthermore, the more effective surfactant topologies enable a strong tail-tail interaction without interfering with the head-water interaction. Surfactants that are shown to effectively reduce surface tension have an effect of widening the interfacial region. The large data set of surfactants used to draw these conclusions was generated using an automated tool. This tool named AutoSurf is a python package designed to facilitate system generation, simulation and analysis of systems containing polymers or surfactants at an interface. The program smoothly integrates user input, python scripts, highly optimized third party open-source
software and post-simulation analysis to enable a standardized methodology by which saturation of the surface and interfacial tension measurements can be obtained through molecular dynamics simulations. The package has been successfully implemented to study over 500 systems containing surfactants with varying topology at a water vapor-liquid interface.
Theoretical Analysis of Interfacial Phenomena during Thin Film Growth and Surfactant Characterization

by
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Chapter 1

Introduction

1.1 Molecular Modeling and Interfacial Phenomena

The motivation for this thesis is to compile and present results from three exploratory studies that advance understanding of interfacial phenomena during atomic layer deposition for electronic fabrication as well as at the surfactant-mediated water vapor-liquid interface using molecular modeling techniques. Additionally, we present the automated tool used to generate data for the scientific exploration of topological effects on the surfactant-mediated water vapor-liquid interface.

Interfacial phenomena is of great importance in a large scope of fields including pharmacology, petroleum recovery, electronics device fabrication, polymer science, flexibility of sensory electronics, catalysis, and bio-medical tools. Understanding the driving forces at the interface is essential in the advancement of these fields. The efficiency of oil recovery in small porous media has been increased using foams that reduce surface tension and increase flow. [21, 20, 40] Electronic device miniaturization has been enhanced using deposition techniques that rely on controlled nucleation at metal and metal oxide
interfaces. Drug delivery uptake and release has become more accurate with increased knowledge of protein transport at phospholipid membranes. [165, 71, 143]

First principle and molecular modeling techniques offer a reliable and optimal approach to study chemical interactions at an interface through an efficient process that significantly reduces the time and cost associated with experimental design and analysis. Molecular modeling approaches are designed to work in coordination with experimental exploration; to be used as guides in chemical design of compounds such as surfactants, or reactants for metal deposition. In addition, molecular modeling has the capability of providing a unique perspective into systems unavailable or inaccessible to experimental exploration due to chemical accessibility, cost, equipment, toxicity or extreme conditions.

Despite significant advances in computational power, many systems containing soft-matter, biological components, etc. or that are behavior-limited within the nanometer scale have tremendous potential beyond the capacity of atomistic simulations. The computational cost of large size/scale systems has been remarkably reduced by using parameters that describe groups, or beads, of atoms versus individual atoms. This concept is called coarse-graining and is two to three orders of magnitude faster in terms of computational effort since it scales according to \( N^{\text{atoms}} \). [122] Coarse-graining has been applied to study systems containing biochemical molecules, such as proteins, lipids and nucleic acids, as well as systems containing soft-matter, such as polymer solutions, liquid crystals, foam and gels. Using this method, long-ranged dynamic correlations between particles can be accurately described. [158, 51]

The surface chemistry between solid state materials and liquid or gas phase components poses a different level of questions since it exhibits characteristics related to condensed-matter physics and chemistry. For instance, a chemical reaction at a metal surface has all of the complexity of ordinary gas-phase reactions, but in addition the solid
surface provides a semi-infinite source of electrons at the Fermi level. Therefore, a new set of concepts needs to be applied to describe these systems, which are highly relevant to semiconductor processing, corrosion, electrochemistry, and heterogeneous catalysis. Electronic structure calculations based on Density Functional Theory (DFT) are increasingly used to probe surface chemistry pertinent to these areas of application. [76] DFT calculations provide invaluable information about geometries, stabilities, and reactivities of adsorbed species on various surfaces. [129, 54] This method has been applied to study systems involving interfacial adhesion, nucleation and growth of organic and inorganic materials, and diffusion. [120, 197, 48]

The broad application of molecular simulations is largely due to the software and force fields that have been developed for the generation, simulation and analysis of soft and hard matter at the quantum, molecular and meso scales. For example, LAMMPS is a molecular dynamics program that has been cited over 13,000 times since its introduction in 1995. VASP is a package for atomic scale materials modeling from first principles that has been cited over 20,000 times since its introduction in 1995. Along with these two packages, numerous tools with broad versatility have been developed to assist in efficiently modeling chemical systems. Success of these tools is highly dependent on the applicability towards various systems, ease of use and continual maintenance. In addition, force fields, such as the SAFT-γ force field developed out of Imperial College under the guidance of George Jackson and Erick Muller, contribute significantly towards the scientific communities ability to accurately model various chemical systems.

At the cornerstone of numerous software and force fields, surfaces and interfaces play a key role in a significant number of research projects conducted by chemists, computational scientists, materials scientists and chemical engineers. The continuous advancement of experimental and theoretical methods used to investigate chemical interactions
at interfaces is essential in promoting scientific discoveries that will continue to revolu-
tionize known and unknown processes. A recurring challenge faced by researchers in
areas of product design, energy and sustainability is the discovery and development of
novel compounds and materials. Materials discovery is a multidisciplinary field that inte-
grates materials science and information sciences to extract and utilize information from
large data sets. Common goals in this field are to discover and design new materials, to
advance knowledge and theoretical understanding of material processes or mechanisms
governing material behavior, to understand the nature of data collection and generation
in both experimental and computational studies, and to develop methods to aid in analy-
sis and interpretation of data. [59] Progress in this field is, by and large, driven by theory,
modeling, and simulation.

This thesis focuses on the use of first principle and coarse-grained molecular dynam-
ics to further understanding of interfacial behavior. The first two projects focus on the
nucleation of various precursors on two commonly used surfaces for atomic layer depo-
sition of thin films for electronic device fabrication and the last two projects focus on
the behavior of surface acting agents (surfactants) at a water vapor-liquid interface and
the method used generate information for 100+ topologies. The purpose of this work is
to demonstrate to readers that current materials discovery methods can be incredibly
advantageous to areas of research including atomic layer deposition of thin films and the
discovery and design of surfactants. As a brief overview of interfacial systems explored
in this dissertation, the following subsections present the motivation and objective for
each chapter. A key aspect in both projects is that, with the integration of modeling
and experimental techniques, we are able to obtain a more complete understanding of
chemical processes and are able to study systems thoroughly and efficiently.
1.2 Tungsten Atomic Layer Deposition

The transformation of electronics following the introduction of the transistor in 1947 has allowed for revolutionary developments in automated equipment, medical fields and research and industrial processes. The ongoing miniaturization of semiconductor device features has allowed for an increasing number of transistors in central processing units (CPUs), which is increasing the amount of computing power at a low cost. Electronic miniaturization cannot simply be viewed as a process to make everything smaller since miniaturization of one component usually reveals limitations and obstacles in other parts of the overall design and manufacturing process. In addition, cutting-edge miniaturization typically becomes more expensive as sizes are reduced, especially considering that a yield of at least 98% is typically necessary to make miniaturization products profitable. [3] Therefore, integrating a new fabrication process for small components requires that the process be as robust, reliable and inexpensive as possible.

Atomic layer deposition (ALD) is a technique that offers enhanced control over thin film growth. This technique is founded on the principle of self-limiting reactions on a substrate surface. In contrast to chemical vapor deposition (CVD), during which two precursors are simultaneously dosed into the system and lead to linear growth, [86] ALD precursors are dosed into the system in sequential, non-overlapping pulses during which the precursor reacts with the surface and the reaction terminates after a single monolayer has formed. For an ideal ALD process, film growth is controlled at the atomic level and after each cycle, the film has grown by the approximate size of the precursor. The ideality of an ALD process is highly dependent on the surface interaction and surface functionality. [12, 27, 49] In research related to thin film growth, precursor options are often limited to what is available or what has been previously tested on related chemical
systems. There is very little deviation from known chemical systems in an experimental setting, for good reason, however, present computational resources offer an unprecedented opportunity to explore the chemical space for precursors that react appropriately in the specific system of interest.

In Chapter 3, we use first principle techniques to identify and quantify reaction paths that lead to nucleation during ALD of tungsten (W-ALD). The numerical data from the first principle models and visualization software has allowed us to explore nucleation reaction mechanisms and provide explanations of the key role that the reactants, WF$_6$ and SiH$_4$, play in the deposition process. Our objective in this project is to demonstrate that computational tools can be used in combination with experimental results to gain fundamental understanding of nucleation during a well-established ALD process. In addition, we discuss the underlying chemistry that drives the self-terminating reactions and the mechanisms that lead to thin film growth on silicon.

Silicon surfaces are typically used for W-ALD and have been a central component in electronic device fabrication due to their moderate energy gap between conduction and valence bands, as well as their high dielectric strength, making them useful for many applications. [36, 35, 105] Tungsten films are widely used for the fabrication of integrated circuit devices due to their electro-migration resistance. In the ALD process, tungsten is deposited by the reduction of tungsten hexafluoride (WF$_6$) using hydrogen (H$_2$), silane (SiH$_4$), Si-H units, or a combination as reducing agents. [79] Reduction of tungsten using silicon as the reductant has been shown to occur by the following reaction:

$$WF_6 + Si-H \rightarrow SiWF_x + SiHF_x + H_2 \quad (1.1)$$

According to experimental results, silane is essential for stripping tungsten of its
fluorine atoms and deposition of tungsten is temperature independent in the temperature range of 200-300°C, indicating that, in this range, there is a negligible activation barrier for chemisorption of WF₆ on the Si-H surface. W ALD on a silicon substrate is split into two half-reactions, where the subscript ‘s’ represents a species bound to the surface:

\[ \text{WF}_6 + (\text{W-Si-H})_s \rightarrow (\text{W-W-F})_s + \text{SiF}_x + \text{HF/H}_2 \]  \hspace{1cm} (1.2)

\[ \text{SiH}_4 + (\text{W-W-F})_s \rightarrow (\text{W-W-Si-H})_s + \text{HF/H}_2 \]  \hspace{1cm} (1.3)

Both of the reactions in Equation 1.2 and Equation 1.3 are thermodynamically favorable according to experimental results. The reaction energetics and activation barriers for the above reactions are further discussed in 3.

1.3 Area-Selective Atomic Layer Deposition

Area-selective atomic layer deposition (AS-ALD) is an enhancement to the original ALD process that incorporates the concept of patterning through an inherent attraction of precursors towards one material versus another. [75] AS-ALD is rapidly gaining interest because of its potential application in self-aligned fabrication schemes for atomic-scale processes. Patterning functional material is a crucial step in semiconductor integrated circuits (ICs) and it has enormous benefits, including controlled and reproducible patterns that can come from self-aligning techniques.

Advancement of AS-ALD processes can be assisted through the integration of ab initio kinetic and thermodynamic analyses with experimental results. These systems are especially susceptible to limitations in comparison to one substrate ALD processes since
the complexity of the system is increased. Specifically, the system requires a chemically selective process to achieve high-resolution thin films through intrinsically selective adsorption behavior of gas-phase reactants on different surfaces. Therefore, the accuracy of this process is dependent on the self-limiting nature of two reactants on one surface, as well as the selective interaction of two reactants on one surface versus another. The high level of complexity of this system further justifies the integration of computational methods.

In Chapter 4, we explore nucleation reactions on silicon as well as hydroxyl-terminated silica. Silica is widely used in the electronics industry due to its high reactivity, tunable electronic properties, low cost, ease of manufacturing, and the unique property of a stable oxide layer. [137] Using these two surfaces, we investigate mechanisms that govern nucleation and selectivity for two ALD systems that are of interest for AS-ALD. The first is the inherent selectivity of TiCl₄ and H₂O towards hydrogen-terminated silicon and hydroxyl-terminated silica. The second is the inherent selectivity of WF₆ and SiH₄ towards hydrogen-terminated silicon and hydroxyl-terminated silica. For these systems, our goal is to calculate the reaction energetics to determine whether the equilibrated state the surfaces after chemical adsorption of a gas-phase reactant is thermodynamically feasible and whether an there is inherent energy difference between two possible gas-phase reactants. For example, the below reactions are explored in this chapter.

\[
\text{SiH}_4 + (\text{Si-O-H})_s \rightarrow (\text{Si-O-SiH}_3)_s + \text{H}_2 \quad (1.4)
\]

\[
\text{SiH}_4 + (\text{Si-H})_s \rightarrow (\text{Si-SiH}_3)_s + \text{H}_2 \quad (1.5)
\]

The reactivities of the two surfaces are strongly dependent on surface features and
system conditions. For example, surface hydroxyl groups on silica play a key role in the nucleation reactions. The reactivity of the surface is highly dependent on the concentration and distribution of hydroxyl groups since the acidic and basic nature of the metal oxide changes with varying concentrations. In the case of AS-ALD of WF$_6$ and SiH$_4$, the non-growth area (NGA) is hydroxyl-terminated silica. A perfect AS-ALD process would show no growth on the non-growth area. However, undesired nucleation is the limiting factor in developing successful AS-ALD processes. By calculating reaction energetics for gas-phase reactants with two surfaces, we will be able to propose the probability at which nucleation occurs on each surface and thereby, quantify the likelihood that AS-ALD can be achieved for that specific system. By demonstrating an atomistic understanding of native selectivity through first principle techniques can invoke investigation of a wide variety of AS-ALD systems through a similar process and lead to advancements in novel systems.

1.4 Coarse-Grained Dynamics of Surfactants

Surface-active agents, or surfactants, are a diverse group of chemicals that alter the interfacial properties between liquids, solids, and/or gases. They are composed of a polar head group (either charged or uncharged) and a nonpolar or hydrophobic tail group, which can consist of hydrocarbon or fluorocarbon groups. Surfactants are widely used in household and industrial products, such as detergents, antiseptics, cleaners, and dispersion agents. Currently, the global surfactant market has exceeded 15 megatons per year and is expected to increase markedly in the following decades. This mass production along with the under-regulated disposal [144] has brought upon the investigation of key surfactants to determine their environmental impact. Additionally, surfactant technology represents
a vibrant and challenging area of physiochemical science where the exact mechanisms of well-established processes are often not fully understood.

Alcohol Ethoxylates (AE’s) are the most common group of nonionic surfactants and are classified as easily biodegradable compounds. [177] Their main application is in washing powders and liquids, cleaning products and cosmetics. Studies on the surface activity of AE surfactants may be helpful in determining applicability and contribute to the development of technical specifications for future applications in many different industries that use surfactants.

A large portion of manufactured surfactants, due to their applications as detergents, cleaners, and personal products, find their way into sewage treatment plants. Since they are hard to remove using conventional water treatment methods, they get dispersed through effluent discharge into surface waters and sludge disposals on land. Research on the fate and effects of various surfactants and their degradation products is in its early stages, with current results suggesting that the mainstream surfactants may be environmentally persistent and a hazard to our ecosystems. [193] Along with the demand to understand their environmental fate, there is also a strong drive towards discovering new, highly efficient, biodegradable surfactants for existing and novel applications. Water is classified as one of the most important liquids in nature and is the most common solvent in biological and industrial systems. Modeling surfactants at an aqueous interface will provide the most accurate results since an accurate description of the properties at water have been the focus of research efforts for more than a century. [109]

There are two measures by which the quality of a surfactant is determined: its effectiveness, which is the ability of a surfactant to lower the surface tension, and its efficiency, which is the concentration at which micelle formation occurs called the critical micelle concentration (CMC). These measures are influenced by both the chemical composition
and the size of the head and tail groups. The influence of molecular structure on interfacial properties has been an area of interest for a few decades. [183, 185] Correlations between surfactant properties and effectiveness/efficiency have been established for entire molecule descriptors (dipole moment, surface area, etc.), as well as for head and tail group structures. [25, 10] However, recent results suggest that progress can be made by focusing more closely on the hydrophobic tail region, a focus which has lead to the design of CO$_2$-philic surfactants with increased surface wetting properties. [1, 42, 132, 190] Expanding applications of CO$_2$ is of significant importance since it is plentiful and has the beneficial properties of being nontoxic and nonflammable. However, since it is a weak solvent, CO$_2$-philic surfactants are needed to improve the quality of CO$_2$. [117] One major development in the field of CO$_2$-philicity and surface wetting capability is the incorporation of fluorocarbon chains, which promotes a very low surface tension between CO$_2$/water and solid surfaces in comparison to linear hydrocarbon tails. However, these surfactants, some of which are now being mass-produced, are expensive and are suggested to be an increased threat to the environment in comparison to hydrocarbon surfactants. Recently, there has been a spike of interest in branched surfactants due to the belief that these systems match the effectiveness of fluorocarbon surfactants without the expense or detrimental effects. [117, 43, 190] The biodegradability of branched surfactants is a matter of concern and has been a deterrent for previous investigators, but the introduction of fluorinated surfactants has reinforced the need for further investigation of hydrophobic structures. [185]

It has been suggested that chain branching gives rise to two beneficial effects that lead to better performance than linear surfactants: first, branching reduces the effective thermodynamic carbon number [99, 114, 149], which increases water solubility by reducing repulsive interactions. Second, by increasing the density of packed, disordered surface
layers at the interface, branched surfactants mimic the structure of neat hydrocarbon oil, which has a naturally low surface energy [1]. The premise behind this research is that water-soluble, low-surface energy hydrocarbon surfactants can be obtained by maximizing the van der Waals interactions and minimizing the hydrophobicity by using branched tail structures. [1, 33, 43, 190]

In recent studies, branched surfactants, such as the Guerbet type, [185] have given rise to good environmental properties, including lower aquatic toxicity and easy biodegradation. Furthermore, experimental results suggest that branched surfactants lead to low foaming and good cleaning performance. However, the structure-performance relationship is not well understood. With various research groups exploring the use of branched surfactants for super-hydrophobic material production and enhanced oil recovery, [33, 190] there is demand for a thorough understanding of how branching influences surfactant efficiency as well as techniques to discover branched surfactants for various applications.

In chapter 5 coarse-grained molecular dynamics and data analysis techniques are used to develop relationships linking surfactant topological features to surface tension reduction and surface saturation.

In terms of simple geometry, it is possible to create many different types of branched surfactants. A few have been experimentally investigated and can be seen in the work of Eastoe et al. [1, 116, 118] To study surfactants with various topological features in an efficient manner, we used coarse-grained molecular modeling to develop a database of 100+ surfactants that fall into the subcategory of nonionic alcohol ethoxylates. By narrowing our chemical scope, we were able to formulate relationships between specific structural features and the ability to pack at the interface and reduce the surface tension. The objective of this chapter is to present the method used to identify the surface
saturation concentration and surface tension reduction.

1.5 Automated Generation of Molecular Models

Scientists, when given a large data set, want to query, explore and visualize the data. A desire that tends to arise during any exploratory journey is the ability to automate discovery, reproduce and retrieve results using very basic computer programming skills. This is often achievable using software that has been effectively written by software engineers and/or scientific programmers. A difference between scientific programmers and software engineers is the importance of generalized functionality to the development of an automated tool. Software engineers tend to view generalization as paramount and central to the process, whereas scientific programmers tend to write code that is specific to the data that drove the analysis. There likely exists countless automated programs for scientific analysis that have have been effectively used as exploratory tools to drive discovery in their field. These tools can be used to leverage further scientific discoveries through a collaborative effort with a team of software engineers that are capable of abstracting code and making it reusable by the broader audience. Research is becoming increasingly computational in nature and it will become increasingly important that scientific code does not end its development cycle after publication of the generated data or visuals. Providing information on the computational tools that were used in data exploration is a first step towards creating robust, reproducible and sustainable software.

The motivation for scientific programmers should not be to create a robust software, but to make their program easily accessible to the software engineer community. The ability to create a modular, robust and reusable software program falls into a field of its own and should not be a requirement for computational research scientists. However, it
should be highly regarded as an essential aspect in accelerating future scientific advances. Therefore, the responsibility of scientists should be to make computational tools essential for their discoveries readily available in the publication of their scientific data. [69, 30, 65]

In chapter 4 we present the automated tool used to generate the data set of surfactants analyzed in the previous chapter. Using the programming language, python, we have designed a reusable program that can be used to study the interaction of surface-active molecules or polymers at an interface. The program goes through a series of steps to generate geometry files, run a series of coarse-grained molecular dynamics simulations and analyze the generated data. With further development and generalization, this program can be further used to advance understanding of polymer-like or surfactant-like molecules at an interface and to create an automated tool for exploring new molecules.

1.6 Novel Contributions

Using molecular modeling approaches, we were able to address the interfacial systems introduced above in a unique manner that led to the following contributions:

1. We provide novel insight into the thermodynamic and kinetic reactions involved in atomic layer deposition of tungsten using WF$_6$ and SiH$_4$ as gas-phase precursors and Si(100) and W(110) as substrate surfaces.
2. We introduce a computational approach by which to gauge the success of ALD systems for area-selective ALD using energetics derived from density functional theory.
3. We perform a topological analysis of surfactants using a database of over 100 structures.
4. We present an automated tool that was used to generate, simulate and analyze thermodynamic properties of systems containing over 5,000 coarse-grained beads.
1.7 Summary

This dissertation provides details on the novel contributions as well as the approach and significant conclusions drawn during each study. The following chapter provides details on models and methods that were used for each project. The rest of the paper is organized into four chapters that address the projects introduced in this chapter. They appear in order of Chapter 3, Tungsten Atomic Layer Deposition; Chapter 4, Area-Selective Atomic Layer Deposition; Chapter 5, Coarse-Grained Dynamics of Surfactants; and Chapter 6, Automated Generation of Molecular Models.
Chapter 2

Methods Overview

2.1 Density Functional Theory (DFT)

In first principle quantum mechanical approaches, the total potential energy surface is determined by solving the Schrödinger equation using the Born-Oppenheimer approximation where the electron density is solved at each iteration. This approximation makes it possible to predict the properties of clusters of over 100 molecules, allowing for an exploration of a variety of systems including organic molecules on metal surfaces, chalcopyrite surfaces, [24] nonequilibrium electron support, [13] perovskites, [47] and atomic layer deposition of metals [164] and metal oxides. [120, 152, 77]

Since the first development of ”density functional theory” in the late 1920’s known as the Thomas-Fermi method, [41] calculating atomic properties based purely on electron density has attracted considerable attention. Dirac extended this theory by incorporating exchange phenomena an extension that is referred to as the Thomas-Fermi-Dirac equation, the basis of the quantum theory of atoms, molecules and solids. Significant contributions were made to the density functional theory in the following decades by
Wigner and Seitz, Slater, Feynman, Hohenberg, Kohn and many more notable scientists. Due to their collective efforts, DFT calculations are now well-established and frequently used in the study of condensed physics and chemistry. [29, 63, 87, 167, 166, 41, 41, 160, 13] The quality of the description of microscopic behaviour from a DFT simulation largely depends on the choice of functional and basis set used. [76]

2.1.1 DFT Exchange-Correlation Functional

The first principle analysis of modern electronic structure calculations is centered around determining the ground-state energy of electrons within molecules. Accurately determining this state for any configuration of the nuclei allows for many properties of the molecule to be found, from bond length and angles, to bond dissociation energies and transition barriers. In first principle calculations, the only information extracted from experimental analysis is the nuclei and number of electrons. From there, the electronic structure of the molecule is solved \textit{ab initio}. However, a direct solution of the Schrodinger equation for the electrons in the molecule is computationally demanding. Therefore, the density functional theory was developed to minimize the computational expense of solving systems of non-interacting electrons by defining them using a one-electron density, which is, in principle, an exact approximation and produces the exact ground-state energy and density, but in practice the exchange-correlation must be approximated. The accuracy of the calculations is dependent on the quality of this approximation. Fortunately and unfortunately for DFT users, this has led to the development of hundreds of different exchange-correlation (XC) functionals that are dependent on the chemical system at hand. The number of functionals available is greatly reduced when considering the specific chemical system. For example, the features and formal properties that are
relevant to extended solids are different than those for small molecules, thus the choices of functionals are different. On the other hand, functionals vary from simple to very complex. The lowest rung is the local density approximation (LDA) in which the XC energy density depends on the density at a point and is that of the uniform gas of that density. LDA typically overbinds molecules by $\sim 1$eV, a large error for chemical applications. The next level includes general gradient approximations (GGAs), which are formulas that use both the density and its gradient at each point. Adding this information greatly reduces the bond dissociation energy error and improves the transition state barriers. Although more advanced functionals exist, we have chosen to use a version of the GGA as the XC functional for our calculations in this thesis. This approximation serves the purpose of allowing us to compare reaction energetics, while also minimizing the computational expense associated with large-scale first principles studies and more exact functionals. [134, 133, 135]

In addition, GGA functionals come in a variety of flavors including non-empirical, a little empirical and over-empirical. The non-empirical uses only general rules of quantum mechanics and special limiting conditions to determine the parameters in a general form. These are not fit to any molecular properties and, instead, are approximated to satisfy as many exact conditions as possible. All parameters are chosen based on inferences from other theoretical methods. Although it is not the most accurate approximation for molecules or solids, the PBE version of GGA is the most universal functional applied to both molecules and solids. An overview of other functional choices can be found in a review by Rappoport et al. [147]

Using the computer program VASP (Vienna Ab initio Simulation Package) geometry optimization and electronic structure calculations for metal/semiconductor/oxide materials were performed. [89, 90, 91, 92] This program employs a basis set of plane-waves to
solve the Kohn-Sham equations of density functional theory (DFT) in a periodic system, and is commonly used in the electronic structure calculations of surfaces. For the DFT calculations in VASP, the projector augmented wave (PAW) pseudopotentials and plane wave basis sets are used. [9, 93] The exchange correlation energy was calculated using the Perdew-Burke-Ernzerhof (PBE) functional in the general gradient approximation. [133]

The DFT total energy is a function of the number and type of atoms, volume cell and atom configuration. This total energy corresponds to the relative Helmhotlz free energy at 0K. In order to calculate temperature dependent properties of intermediates and transition states, vibrational frequency calculations are needed to estimate state properties of species at finite temperatures via statistical mechanics, which is outside the scope of this thesis. Salciccoili et al. provide an in depth overview of coupling Monte Carlo models with chemical kinetics including detailed information on simulating kinetic phase transitions in model systems. [150, 153]

2.1.2 Reaction Thermodynamics and Kinetics

The ability to control chemical reactions at the atomistic level depends critically on being able to describe elementary reaction steps from reactants to transition state to products. This ability allows us to predict the work-flow of chemical transformations and to develop methods to direct chemical reactions towards more selective pathways. In the past two decades, the development of computational chemistry using density functional theory has contributed significantly to the clarification of mechanisms and transition-mediated reaction paths for nucleation and deposition of metals and semiconductors.

Reaction thermodynamics and kinetics calculations can be carried out using slab or cluster models of the surface in conjunction with plane-wave density functional theory.
Previous research studies have shown an appreciable difference between activation energies calculated using slab and cluster models. The slab-model, in the case of H\textsubscript{2} desorption on Si(100), gave activation energies that are close to experimental values. Generally, it is significantly more difficult to design a cluster model that accurately represents the system and predicts structural properties that are comparable to experimental results. [124, 67] All DFT calculation shown in this thesis were performed using periodic slab models.

Using VASP as the quantum mechanics calculator, crucial points along the reaction pathways, such as minima and transition states, can be located enabling the investigation of reaction mechanisms in great detail. The success of the reaction rate calculation methods is strongly dependent on accurate approximations of the stationary points on a reliable potential energy surface (PES) and the number of configuration along the reaction coordinate. In this thesis, the zero temperature string method (ZTSM) was used to determine the lowest energy path for the rearrangement of a group of atoms from one configuration to another. This method works by using a discretized string that is connects reactant and product through an interpolation of the atomic coordinates. The forces are calculated for the atoms in each configuration across the reaction coordinate and are used to manipulate the string in the direction of the force on each structure according to Newton’s law of motion. The string is then reparametrized and configurations are spaced across the string to ensure that the entire reaction pathway is represented. This process is repeated until the pathway has converged to a minimum energy path on the potential energy surface. The transition state configuration and rates for complex systems can be determined efficiently using this method. The reader is referred to references [31, 138] for further details on the method.

Using DFT in coordination with ZTSM provides information across the reaction co-
ordinate of a chemical reaction, i.e. reaction, transition state and product geometries and associated energies. While the rate of a reaction depends just on the activation energy, the final ratios of products in chemical equilibrium depends only on the standard free-energy change. However, the Hammonds postulate states that the molecular reorganization of structural features has to be small during a reaction process and have nearly the same energy content. For example, in an exothermic reaction, the transition state is closer in energy to the reactants, whereas in an endothermic process, the transition state is closer in energy to the products. In addition, the Brønsted-Evans-Polanyi principle states that the difference in activation energy between two reactions of the same chemical composition is proportional to the difference of the enthalpy of the reaction. This serves as an efficient means by which to analyze a chemical system with more than one available reaction pathway. Applying this principle, would reduce repeating activation barrier calculations for reactions that have the same reactant or products. This is especially useful for studying deposition processes, since many different surface reactions are typically available for a single precursor. \[37, 58\]

Provided the reaction mechanisms and rate constants are known for a system, the spatial configuration over a nanometer scale can be modelled as the collective behavior of the ensemble of all species. At the mesoscopic scale, the collective behavior is averaged over the length and time scales that are much larger than the characteristic length and time scale of the underlying pattern used to calculate the reaction rate. Due to the fast vibrations of adsorbates with respect to the reaction time scales, adsorbates are typically thermally equilibrated and reaction events are rare events, i.e. over the time scale of a chemical reaction. The Kinetic Monte Carlo (KMC) method is the most commonly used statistical technique for averaging spatiotemporal events. \[11, 15\] This method is outside the scope of this work, but can be applied in conjunction with DFT/ZTSM calculations.
2.2 Coarse-grained Molecular Dynamics

A step up from the first principle quantum mechanical approach is the classical atomistic level of description, which can employ experimental data or quantum mechanical data to parametrize each atom explicitly.

There are a plethora of options in designing coarse-grained models. One being the mapping of all-atom or united-atom classical force fields (bottom-up) or the use of experimental data for the bulk-phase thermophysical and structural properties (top-down) to parametrize pairwise additive potentials. [125] The top-down approach makes use of analytical functions to provide a simplified classical representation of repulsive, dispersive and electrostatic interactions, whereas the bottom-up approach makes use of all-atom scale calculations to develop interaction parameters. The integration of models across time and length scales enables top-down modeling, in which optimization targets can be defined (e.g. maximum activity and/or selectivity), to be useful in performing searches for materials with suitable properties. This capability opens up a plethora of opportunities for product design.

Coarse-grained (CG) methodologies are used to develop simple intermolecular potentials for large-scale systems. Coarse-grained systems are less physically detailed potential models in which interactions are represented in a highly simplified, but effective manner. The use of CG models has gained much popularity in recent years due and is driven by the desire to simulate increasingly large systems for longer times. [102, 125, 28, 84] Many processes important to interfacial chemistry have cooperative effects that cannot be described accurately using atomistic representation. There is substantial gap between timescale and spatial scale that govern typical intermolecular events that are relevant. Figure 2.1 illustrates the timescales and length scales available to specific systems. Coarse-
graining reduces the level of detail in the representation of the system while retaining a close connection to the underlying atomistic representation and allowing the study of events that occur on timescales of hundreds of seconds to nanoseconds to milliseconds and spatial scales of microns. This method has gained widespread usage in polymer and biophysical communities. The most common motif employed in many models is the lumping groups of atoms together into a single interaction site. As an example, for amphiphilic molecules, the head group is composed of polar chemistries (-O-, -OH) and the tail group is composed of nonpolar chemistries (-CH$_2$-, -CF$_2$-). The coarse-grained force fields are used directly in Molecular Dynamics (MD) simulations in order to explore dynamical, structural and interfacial properties. In this study, we employ the SAFT-$\gamma$ Mie coarse-grained force field to describe systems comprised of non-ionic surfactants and water. [Lobanova, thesis] This methodology has been shown to provide an accurate representation of vapor-liquid properties and allow for a prediction of key structural and interfacial properties. Molecular dynamics simulations of non-ionic surfactants reveal the spontaneous formation of micelles at low surfactant concentrations and a self-assembling bilayer at high surfactant concentrations. The aggregation number, critical micelle concentration, area per molecule, surface excess properties and bilayer thickness were all found to be in very good agreement with experimental data. [101, 104, 103, 102, 146]

Molecular Dynamics uses Newton’s equation of motion to move the coarse-grained beads according to their intermolecular forces.

$$ F_i = m_i a_i = m_i \left( \frac{d^2 r_i}{dt^2} \right) = -\frac{\partial U}{\partial r_i} \tag{2.1} $$

where $m_i$, $a_i$ and $r_i$ are the mass, acceleration and position of particle $i$. Using Equation 2.1, new positions and velocities are determined based on the forces acting on the
Figure 2.1: Schematic of various models operating at increasing time and length scales. Redrawn from reference [15].
particles. The equation of motion is commonly integrated numerically using the Verlet’s algorithm or a modification to the algorithm, such as the leap-frog. [186] For both cases, new positions are obtained from the previous position and acting force. Using Newton’s equation of motion and Verlet’s integration algorithm, equilibrium properties can be calculated for an equilibrated system.

2.3 Scientific Coding

2.3.1 Python

Many scientists and engineers use R and MATLAB to solve data analysis and data science problems. Python, however, is an open source code [8] as well as a general-purpose, high-level programming language. In combination with specialized modules, such as Numpy, Scipy, and Matplotlib, python is robust programming language for solving numerical problems in scientific computing. Python is also capable of all of the complex techniques that advanced programmers expect, like object orientation. Furthermore, the community of Python is large and quickly growing. A major advantage is that many common mathematical and numerical expressions have been pre-compiled into two packages and be easily incorporated. The NumPy (Numeric Python) package provides basic routines for manipulating large arrays and matrices of numeric data and the SciPy (Scientific Python) package includes useful algorithms, such as minimization, Fourier transformation, regression, and other applied mathematical techniques. These packages are also open source and are comparable to commercial packages like MatLab. [8, 182]

Due to the ease of use and the resources available online., Python, along with NumpPy and SciPy, was used to develop the automated tool used to analyze over 500 surfactant
systems containing over 5,000 coarse-grained beads. The python tool will be discussed in further detail in Chapter 6.
Chapter 3

Ab initio Analysis of Nucleation Reactions during Tungsten Atomic Layer Deposition on Si(100) and W(110) Substrates

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3.1 Abstract

We present a detailed analysis using density functional theory to provide novel insight into the mechanisms that govern nucleation during tungsten atomic layer deposition (W-
Along with intensive experimental data, we use calculated energetics to suggest the most probable series of reactions that lead to monolayer formation on desired growth surfaces, Si(100) and W(110), during sequential doses of WF\(_6\) and SiH\(_4\). From our analysis, we conclude that a relatively high-energy barrier exists for initial nucleation of WF\(_6\) on a silicon substrate; therefore, the system is limited to physical adsorption and is only capable of accessing nucleation pathways once the reaction barrier is energetically accessible. During early doses of WF\(_6\), the initial silicon surface acts as the reductant. Results from this half-reaction provide support for non-coalesced growth of initial W layers since nucleation is shown to require a 2:1 ratio of silicon to WF\(_6\). In addition, release of H\(_2\) is significantly favored over HF production leading to formation of fluorine-contaminated silicon sites; etching of these sites is heavily supported by the absence of fluorine observed in experimentally deposited films as well as the high volatility of silicon-subfluorides. In the second half-reaction, SiH\(_4\) plays the multipurpose role of stripping fluorine atoms from W, displacing any adsorbed hydrogen atoms and depositing a silicon hydride layer. Saturation of the previously formed W layer with silicon hydrides is a crucial step in depositing the consecutive layer since these surface species act as the reductants in the succeeding dose of WF\(_6\). The SiH\(_4\) half-reaction reaches a limit when all fluorine atoms are removed as silicon subfluorides (SiF\(_x\)H\(_y\)) and tungsten sites are terminated with silicon hydrides. The WF\(_6\) dose reaches a limit in early doses when the reductant, i.e. the surface, becomes blocked due to the formation of a planar network of fluorine-containing tungsten intermediates and in later cycles when the reductant, i.e. adsorbed silicon-hydrides, are etched entirely from the surface. Overall, the calculated energetics, along with experimental evidence, indicate that WF\(_x\)H\(_y\), SiF\(_x\) and H\(_2\) molecules are the most probable by-products released during the ALD process. Results from this work contribute significantly to the fundamental understanding of atomic layer growth of tungsten using ALD.)
silicon species as reducing agents and may be used as a template for analyzing novel ALD processes.

3.2 Introduction

The semiconductor industry is actively focused on developing atomic layer deposition (ALD) techniques for insulating, semiconducting and conducting materials that allow for atomically thin device layers with defect-free film composition. Using ALD, single atomic layers can be deposited allowing for enhanced control of thin film growth and a means by which to reduce the restrictive 7-nanometer node size available to the industry. [17] Well-established ALD processes exist for specific chemical systems and are currently employed in the semiconductor industry for the deposition of metal thin films for source and drain contacts, gate dielectrics, and in the deposition of seed layers for Damascene metal deposition in interconnects and vias. [126, 128] However, the potential for ALD application remains abundant and is contingent on increasing the accuracy of existing half-reactions and development of novel processes. Using existing ALD half-reactions, atomistic studies can be used to thoroughly understand self-limiting mechanisms in order to increase the accuracy of current processes and create a template by which to design new processes for desirable materials.

Tungsten ALD (W-ALD) is an example of a well-established process that is currently employed in the semiconductor industry. Deposition of W via silane reduction was first confirmed in 1987 at a high deposition rate in a low temperature range, [188] and after nearly two decades of extensive research on W chemical vapor deposition (W-CVD), George et al. demonstrated deposition of W using sequential doses of WF₆ and Si₂H₆. [83] Their successful validation of self-limiting surface reactions led to a new ALD process
for tungsten that offered enhanced control of composition, thickness and conformality. [83, 38] Tungsten is a highly desirable material for its properties, such as resistance to high temperatures, hardness, high thermal and conductive properties and chemical inertness to oxidation, so the ALD process is widely used in contact and diffusion barriers, low resistance gates and interconnect lines in a VLSI circuit and continues to be developed for applications in Area-Selective ALD (AS-ALD) and as a template for novel chemistries. [2, 50, 169]

The most common tungsten ALD and CVD processes use tungsten hexafluoride, which can be reduced by silane, hydrogen or crystalline silicon surface sites, with silane and crystalline silicon being the most commonly used due to their high-rate, low-temperature process conditions. Despite the numerous studies on tungsten ALD/CVD, the physicochemical characteristics that control tungsten growth have yet to be sufficiently described and the chemical pathways that drive deposition remain contested; an example being the disputed emission of HF and tungsten subfluorides. [35, 56, 195] In addition, the self-limiting half-reactions are often described using a single reaction mechanism with unspecified stoichiometry, while in reality the half-cycles proceed through a series of unidentified sub-reactions. Furthermore, deposited thin films have a high surface-to-volume ratio making an atomistic understanding of surface chemistries crucial in increasing the accuracy and efficiency of the existing process.

In this paper, we present an ab initio analysis of the W-ALD process in order to enhance understanding of nucleation phenomenon and provide a unique perspective into the specific chemistries that influence monolayer growth. Using density functional theory (DFT), we perform a systematic exploration of potential reaction pathways to identify the most probable reactions that lead to nucleation during the W-ALD self-limiting half-reactions. DFT is a standard quantum mechanical method that is often applied to systems
involving metallic and semiconducting materials [63] in which experimental studies, such as W-ALD, are limited by inconsistent results and non-equilibrium conditions. [100, 152, 164] This study focuses specifically on W-ALD using WF$_6$ and SiH$_4$ as precursors and selectively-terminated Si(100) and W(110) as substrate surfaces.

This work is organized as follows: the methods section provides DFT and reaction pathway calculation parameters as well as the method used to generate geometry files; the results and discussion sections are organized sequentially according to corresponding half-cycle. The results section provides details on identified reaction mechanisms and the discussion section provides an analysis of the results in light of experimental evidence.

### 3.3 Simulation Methods

We performed calculations using the ab initio plane-wave pseudopotential approach as implemented in the Vienna Ab-initio Simulation Package (VASP). [89, 92] The Perdew-Wang (PW91) functional was used to perform periodic DFT calculations with valence electrons treated explicitly. Interactions within the ionic cores were described using the projector augmented-wave (PAW) method, which allowed for an energy cutoff of 400eV to be specified. The gamma point was used in the Brillouin-zone integration with a 6x6x1 k-point mesh, and the positions of all atoms were relaxed self-consistently until the total energy difference decreased below $10^{-4}$ eV.

Hydrated-silicon (Si(100)-H) and fluorinated-tungsten (W(110)-F) slabs were used to imitate surfaces available during tungsten ALD. To prepare the slabs, the unit cells of the substrate were allowed to relax in volume, shape, and atomic coordinates. The unit cell was then replicated and cleaved along a given Miller plane and vacuum was added above and below the slab to create a semi-periodic simulation. The mid-section
atoms were frozen to approximate bulk substrate and, in some cases, the surface atoms were passivated to eliminate dangling electrons. Finally, surfaces were relaxed into their ground state.

Interaction energies were calculated for surface interactions using the general equation:

\[
\Delta E_{0,\text{Interaction}} = [E(0,\text{Slab}) + E(0,\text{Precursor})] - [E(0,\text{Slab}+\text{Adsorbant}) + E(0,\text{by-products})]
\]  (3.1)

The reaction mechanisms and rates were calculated using the zero-temperature string method (ZTSM). This method is an interpolation algorithm that requires both reactant and product configurations to generate a sequence of configurations along the reaction coordinate. [31, 139] The coordinates of the generated configurations are connected by a string that is optimized during the reparametrization step in the direction of the force normal to the string. The sequence of configurations is then regenerated along the optimized string. The bulk of computational time required is due to the cost associated with calculating forces on each atom in the system, which are used during the reparametrization step. This cost can be reduced by freezing bulk atoms in the slab. One particular advantage of ZTSM is the ability to choose the parametrization density, or the spacing of configurations on the reaction coordinate, based on intrinsic properties that are relevant to the system at hand. In this particular study, we used two reparametrization conditions in order to develop a more descriptive representation of the reaction pathway: an equal spacing and energy-weighted spacing of the configurations Figure 3.1.

The reaction path was divided into 12-15 configurations, depending on the complexity of the reaction. The time-step for numerical integration of the equation of motion during the reparametrization step was chosen so the maximum change in atom position was 0.05Å.
3.3.1 Surface Model Descriptions

Adsorption was performed on the (100) plane of silicon A4 diamond since it is known to have the lowest surface energy (1.28 eV/Å²) and the semiconductor industry typically...
works on this surface. The supercell dimensions for the silicon substrate were 11.57Å/ x 11.57Å/ x 19.12Å/, which was equivalent to 3x3x5 unit cells. The substrate contained a slab of 12 layers thick with 108 silicon atoms and 36 surface hydrogen atoms and the system contained the equivalent of two unit cells (7.72Å) of vacuum. The top half of the hydrogen-terminated silicon (100) surface is represented in Figure 3.2.

Figure 3.2: Top half of a seven-layer silicon slab with 100 orientation and hydrogen passivation: silicon atoms (dark grey) and hydrogen atoms (white). Periodic boundary conditions were employed to approximate bulk substrate.

Tungsten was modeled as a body-centered cubic (BCC) lattice using a supercell with dimensions of 9.51Å/ x 13.45Å/ x 17.71Å/, which was equivalent to 3x4x5 unit cells. The substrate contained a slab of 7 layers with 63 tungsten atoms and 18 surface fluorine atoms with the equivalent of 3.5 unit cells (11.06Å/) of vacuum. Adsorption was performed on the W(110) surface since this surface was identified by Jain et al. to have the lowest surface energy versus W(111) and W(100). [73, 179] The top half of the fluorine-terminated tungsten surface is represented in Figure 3.3.
3.4 Results

The standard W-ALD process proceeds through the following steps: WF$_6$ is exposed to hydrogen-terminated silicon with 100 orientation to produce surface tungsten fluorides; the system is purged to remove unused reactants and gaseous by-products; SiH$_4$ is exposed to the tungsten fluoride surface to produce silicon hydrides, analogous to the starting Si-H surface; the system is purged to remove by-products. These steps, illustrated in Figure 3.4, result in tungsten growth and are repeated until desired film thickness is achieved.

3.4.1 Nucleation of WF$_6$ on hydrogen-terminated Si(100)

During the initial dose of WF$_6$ onto a hydrogen-terminated silicon (Si(100)-H), the overall, unbalanced reaction can be expressed as:
\[ Si(100) - H_{(s)} + WF_{6,(g)} \rightarrow Si(100) - WF_aH_{b,(s)} + SiF_xH_y{(g)} + H_{2,(s)}/HF_{(g)} \] (3.2)

In reality, the above reaction proceeds through an unidentified number of sub-reactions. Using elementary reaction steps, we identify these sub-reactions, as well as intermediate species that exist during nucleation on Si(100). The identified species and calculated energy differences for each elementary step are shown in the overall schematic in Figure 3.5. This reaction cascade, detailed through this section, illustrates the pathways identified as thermodynamically probable, indicated by black arrows, and less probable, indicated by red arrows.

As depicted in the first step in Figure 3.5, upon introduction of WF$_6$ to hydrogen-terminated silicon (100), two elementary reactions are available to the system. These
reaction mechanisms along with corresponding energy differences and activation barriers are presented in R1 and R1.hf. Reaction labels including hf, i.e. R1.hf, denote alternate
reaction paths that result in HF production, while those including a denote an alternate path for the same reactants.

\[
H - Si(100) - H + WF_{6,(g)} \rightarrow H - Si(100) - F + WF_5H_{(g)} \quad \Delta E = -0.34, E_\ddagger = 2.01 \quad (R1)
\]

\[
H - Si(100) - H + WF_{6,(g)} \rightarrow H - Si(100) - WF_5 + HF_{(g)} \quad \Delta E = +0.93, E_\ddagger = 2.76 \quad (R1.hf)
\]

where the given energy values are in eV. For both pathways, WF\textsubscript{6} physisorsbs onto the surface with a binding energy of -0.52eV. From this state, the ligand exchange re-
action, forming WF\textsubscript{5}H (R1), is exothermic (\(\Delta E = -0.34eV\)) with a barrier (\(E_\ddagger\)) of 2.01 eV, and is therefore more favorable than the reaction producing HF (R1.hf) which is endo-
thermic (+0.93eV) with a barrier of 2.76 eV. The pathway for reaction R1, producing
WF\textsubscript{5}H\textsubscript{(g)}/Si-F\textsubscript{(s)} is depicted in Figure 3.5 as a solid black arrow.

Following reaction R1, WF\textsubscript{5}H can further react with a hydrogen-terminated site, as
depicted in R2 and R2.a, to produce WF\textsubscript{4}H\textsubscript{2} (R2) or chemisorbed WF\textsubscript{5} (R2.a).

\[
F - Si(100) - H + WF_5H_{(g)} \rightarrow H - Si - F + WF_4H_2_{(g)} \quad \Delta E = -0.25 \quad (R2)
\]
\[
H - Si(100) - H + WF_5H(g) \rightarrow H - Si - WF_5 + H_2(g)
\]
\[
\Delta E = -0.19, E^\ddagger = 1.56
\]

Reactions R2 and R2.a are both exothermic with calculated energy differences of -0.25eV (R2) and -0.19eV (R2.a) with an activation barrier of 1.56eV for reaction R2.a.

In addition, WF\(_5\)H can react similarly with a partially fluorinated site, as depicted in reactions R3 and R3.a, to produce WF\(_4\)H\(_2\) (R3) or chemisorbed WF\(_5\) (R3.a). However, in this case, Reaction 3 is exothermic (-0.39eV) with a barrier if 2.15 eV, whereas R3.a is slightly endothermic (+0.06eV).

\[
F - Si(100) - H + WF_5H(g) \rightarrow F - Si - F + WF_4H_2(g)
\]
\[
\Delta E = -0.39, E^\ddagger = 2.15
\]

\[
F - Si(100) - H + WF_5H(g) \rightarrow F - Si - WF_5 + H_2(g)
\]
\[
\Delta E = +0.06
\]

The product differences between the above four reactions are illustrated in Figure 3.6.

Comparing the above four reactions between WF\(_5\)H and Si(100) (R2, R2.a, R3, and R3.a), we see that WF\(_5\)H is more likely to undergo ligand exchange at either passivation site to produce WF\(_4\)H\(_2\) and is highly unlikely to chemisorb at a partially fluorinated site. Ligand exchange is favored since it results in the formation of an additional surface silicon-fluorine bond, the strongest in the system. Reactions R2, R2.a and R3 are all
thermodynamically probable; however, the activation barrier associated with R2.a is lowest, suggesting that, although production of WF$_4$H$_2$ is thermodynamically favored, both products, chemisorbed WF$_5$ and gaseous WF$_4$H$_2$, will be sampled in the system. A clear difference between R2, R2.a, R3 and R3.a is that adsorption of WF$_5$ is likely to occur on a surface site containing two hydrogen atoms, whereas WF$_4$H$_2$ production is favorable at both sites, with the partially fluorinated site being more favorable. Production of HF is highly unlikely at lower temperatures as supported by R1.hf and parallel endothermic reactions using the products from R1, as shown in R2.hf and R3.hf:

\[
H - Si(100) - H + WF_5 H(g) \rightarrow H - Si(100) - WF_4 H + HF(g) \\
\Delta E = +1.64
\]  

(R2.hf)
For the pathways leading to gas-phase WF$_4$H$_2$ (R2, R3), WF$_4$H$_2$ is unlikely to leave the system as a gas-phase by-product since it strongly physisorbs onto hydrogen-passivated silicon sites with a downhill energy of -1.32eV. Therefore, consecutive interactions between WF$_4$H$_2$ and neighboring hydrogen-passivated silicon sites are likely and may lead to chemisorbed WF$_4$H (R4) or gas-phase WF$_3$H$_3$ (R4.a).

\[
F - Si(100) - H + WF_5H_{(g)} \rightarrow F - Si(100) - WF_4H + HF_{(g)} \\
\Delta E = +1.88
\]

(R3.hf)

\[
H - Si(100) - H + WF_4H_{2,(g)} \rightarrow H - Si(100) - WF_4H + H_2_{(g)} \\
\Delta E = -0.20, E_t = 1.54
\]

(R4)

\[
H - Si(100) - H + WF_4H_{2,(g)} \rightarrow H - Si(100) - F + WF_3H_3(g) \\
\Delta E = -0.01, E_t = 2.20
\]

(R4.a)

Production of H$_2$ and chemisorbed WF$_4$H (R4) has an overall energy difference of -0.20eV with an activation barrier of 1.63eV, while production of gas-phase WF$_3$H$_3$ (R4.a) is less favorable with an overall energy difference of -0.01 and an activation barrier of 2.20eV.

Alternatively, following the divergent pathway involving chemisorbed WF$_5$ (R2.a), can react successively with a neighboring site to form a silicon-silicon surface dimer. The corresponding reaction mechanism is shown in R5:
\[ H - Si(100) - H + H - Si(100) - WF_5 \rightarrow H - Si(100) - Si(100) - WF_5 + H_2(g) \]
\[ \Delta E = -0.13, E^* = 0.78 \]

(R5)

The reconstruction of the silicon site with chemisorbed WF\textsubscript{5} to form a surface silicon dimer is thermodynamically downhill (-0.91eV) with a relatively low barrier (0.79eV).

In both pathways, surface fluorination through ligand exchange reactions promotes etching of silicon sites since it increases volatility of silicon. For further support, we calculated the complete ligand exchange reaction between molecular WF\textsubscript{6} and SiH\textsubscript{4}. The mechanism for the exothermic reaction is shown below.

\[ WF_6(g) + SiH_4(g) \rightarrow SiF_4(g) + WF_2H_4(g) \]
\[ \Delta E = -0.2eV \]  

(3.3)

The downhill energy associated with the above reaction indicates that if fluorine is present in the system, silicon will act as a reductant until saturated with fluorine or purged from the reactor. Once silicon surface sites are removed as volatile subfluoride species, a reactive site will be available for W deposition. Therefore, adsorption of WF\textsubscript{6} on Si(100) may proceed through two pathways: 1) at an unetched site to produce volatile H\textsubscript{2} or HF; and/or 2) at an etched surface site. Notably, W deposition is very unlikely to occur at sites containing fluorine, which are favorably produced according to the above reaction scheme, so these sites are either etched or inactive for the remainder of the ALD process.
3.4.2 Reaction of SiH$_4$ on coalesced, fluorine-terminated W(110)

After nucleation has led to the formation of a fully coalesced tungsten film, SiH$_4$ is dosed into the system and interacts with deposited W (Figure 3.8, bottom half). Crystalline W is therefore used to represent the system surface:
Prior to deposition of WF$_6$ in succeeding half-cycles on a W(110) surface, SiH$_4$ plays an essential role of stripping fluorine content from the deposited W surface. The mechanism for SiH$_4$ reducing fluorine-terminated tungsten (W(110)-F) is shown in R6, with the reaction path and structures shown in Figure 3.9.

\[
W(110) - F + SiH_4(g) \rightarrow W(100) - H_{Bridged} + SiH_3F(g)
\]
\[
\Delta E = -1.43 \text{eV}, \quad E^\ddagger = 0.73 \text{eV}
\]  

(R6)

Figure 3.9: Reaction energetics and structures for ligand exchange during SiH$_4$ exposure on fluorine-terminated W(110).

As depicted in Figure 9, SiH$_4$ favorably reacts with W(110)-F to form SiH$_3$F with a downhill energy of -1.43eV and an activation barrier of +0.73eV. Reduction of W(110)-F proceeds until all fluorine content is removed and leads to increased reactivity at reduced sites (W(110)*), which are exposed to gas-phase SiH$_4$ to form W(110)-SiH$_x$. The reaction between SiH$_4$ and reduced W sites to form W(110)-SiH$_x$ is highly exothermic with an energy difference of -3.16eV. If W(110)* sites and W(110)-F sites are within proximity, SiH$_4$ favors the removal of fluorine from W(110)-F to chemisorption at W(110)*. In addition, SiH$_3$F, produced through a reduction reaction between SiH$_4$ and W(110)-F, can successively interact with the surface and also favors reduction of W(110)-F to chemisorp-
tion at W(110)*. Taking into consideration that SiH$_x$F$_y$ species are present in a much lower concentration than SiH$_4$, and less likely to chemisorb due to the steric hindrance of fluorine ligands, the predominant chemisorbed species at the end of the cycle is likely SiH$_x$ over SiH$_x$F$_y$.

Overall, reduction of fluorine-terminated W via SiH$_4$ is supported by the exothermic reaction shown in the mechanism below:

$$4W(110) - F + SiH_{4(g)} \rightarrow 4W(110) * + 2H_2 + SiF_{3(g)}$$

$$\Delta E = -1.89\text{eV}$$

(3.4)

### 3.4.3 Reaction of WF$_6$ on coalesced, SiH$_x$-terminated W(110)

WF$_6$ nucleates on W(110)-SiH$_x$ after SiH$_x$ is removed from the surface as gaseous SiH$_x$F$_y$ (R7). In the mechanism, the stoichiometry of surface species and products are kept indefinite since several reaction pathways exist:

$$WF_{6,(g)} + W(110) - SiH_x \rightarrow W(110) - WF_aH_b + SiF_{x}H_{y,(g)}$$

(R7)

Terminal SiH$_x$ species become volatile as SiH$_x$F$_y$ through a reduction reaction with gas-phase WF$_6$ leaving reactive surface sites (W(110)*) available to WF$_6$ and WF$_x$ exposure. WF$_x$, a gaseous by-product, is also formed during the surface reduction. WF$_6$ deposits on W(110)* with an overall energy difference of -3.42 eV through a reaction involving a simultaneous reduction via a neighboring W(110)* site, as depicted in Figure 3.10. The formation of W(110)-F leads to loss of reactivity unless a reductant species (SiH$_x$F$_y$) is available to the fluorinated sites. The experimental observation of coalesced films implies that significant W site deactivation must be overcome during deposition or
that the depositing species is the gaseous by-product, WF$_x$. Deposition via intermediate WF$_x$ species would lead to less loss of growth sites per W atom. Based on the calculated results, WF$_5$ and WF$_4$ are likely by-products that react favorably with W(110)*, with WF$_4$ being the favored adsorbent. Figure 10 illustrates the loss of reactivity at W(110) sites through WF$_6$ exposure to form chemisorbed WF$_5$ and WF$_4$.

Figure 3.10: Illustrations of the interaction between WF$_6$ and W(110) (R9): pentafluoride product (top right, -2.63eV) and tetrafluoride product (bottom right, R12, -3.42eV

As previously mentioned, during succeeding SiH$_4$ doses, if W(110)-F sites are present, SiH$_4$ will preferentially extract fluorine before silicon deposition proceeds.

3.5 Discussion

3.5.1 Nucleation of WF$_6$ on hydrogen-terminated Si(100)

According to the calculated reaction energetics, WF$_6$ favorably reacts with a silicon surface site to produce hydrogen gas and, at higher temperatures, hydrogen fluoride, which is in agreement with the experimental observation that HF is only observed above 800K.
The typical ALD process is performed at \( \sim 500K \) and, therefore, HF is not considered vital in the ALD process sequence, \([195, 53, 72, 194]\) leaving one predominant elementary reaction step to produce WF\(_5\)H (R1). The route leading to chemisorbed WF\(_5\)H is significantly favored over the release of HF, allowing us to conclude that tungsten sub-fluoride vapor products contribute to net W deposition. Furthermore, subfluorides are not detected experimentally using thermal desorption analysis, \([72]\) suggesting that they play a substantial role in the deposition process only as reactive intermediate species.

Prior to formation of WF\(_5\)H, WF\(_6\) physisors onto hydrogen-terminated silicon with an energy of -0.52eV; a larger than typical value for physisorption. However, a strong physisorption energy is necessary for the system to overcome the fairly high transition barriers associated with adsorption. These high barriers are supported by the experimental finding that chemisorption of WF\(_6\) is not achieved until the system exceeds 150K. \([72]\) Below this temperature, the energy barrier associated with adsorption (\(\sim 3eV\)) cannot be overcome and interaction is limited to physical adsorption. As the temperature of the system is raised, increased mechanical work and thermal fluctuations contribute to the probability of activation. Once the initial activation barrier is overcome, WF\(_5\)H further reacts with surface sites to produce chemisorbed WF\(_5\) or volatile WF\(_4\)H\(_2\). The favored production of WF\(_4\)H\(_2\) and two terminating fluorine atoms on a single silicon site, along with the exothermic formation of an additional Si-F surface bond, through WF\(_3\)H\(_3\) production, supports formation of volatile SiF\(_x\) species. Formation of SiF\(_x\) (\(x>1\)) surface species promotes etching since silicon is stabilized and becomes volatile upon further fluorination. Etching of silicon from the initial Si-H surface is experimentally supported by observed mass loss during the WF\(_6\) dose \([19, 192]\) as well as the experimental detection of SiF\(_x\) (\(x = 0 - 4\)) above 300K. \([72]\)

In addition to surface etching, dimerization of two Si surface atoms is a well-studied
phenomenon \([57]\) that is energetically feasible during the initial \(WF_6\) dose. This reconstruction would diminish additional reactivity since adsorbed tungsten species would sterically hinder further interaction of adjoined sites. Deactivation of surface sites would support the finding that, at lower cycle numbers (less than 5 cycles), the mass gain is less than the average for the entire growth period. \([38]\) Furthermore, it supports the observed delay in conformal tungsten growth on \(Si(100)\) at lower cycles. \([34, 97]\) Another factor that may contribute to lower than average mass gain in early cycles is the production of stable Si-F surface bonds which are produced through favorable ligand exchange reactions with \(WF_xH_y\). For deposition to proceed at these sites, the stable Si-F surface species must be etched as \(SiF_x\) species, with thepredominantly observed species being \(SiF_4\). Removal of the fluorinated surface sites would create additional availability on the Si surface for W deposition; an etch/deposition mechanism that is supported by Elam \(et\ al.s\) conclusion that during the W-ALD deposition process a silicon layer of approximately equal thickness to the deposited tungsten layer is consumed. \([35]\) However, etching would become slower as nucleation proceeds since the silicon species would be required to diffuse to the surface before being volatilized.

Based on the energetics and experimental evidence, multiple reaction pathways are occurring simultaneously with the likely by-products being \(WF_xH_y\), \(SiF_x\) and \(H_2\). For these reaction pathways, \(WF_6\) must encounter at least two surface silicon sites. Since access to two sites would become limited as \(WF_6\) nucleation proceeds, complete W coverage during early doses would require extended precursor dose times.
3.5.2 Reaction of SiH₄ on coalesced, fluorine-terminated W(110)

Silane plays the essential, but sacrificial, role of stripping surface fluorine atoms to reduce terminal tungsten groups. [83] The reduction is highly exothermic (R7, -1.43eV) due to the formation of strong SiF bonds and H2 and SiF₄ make up the majority of the products evolved. [194, 195] As long as fluorine is available on the surface, SiFₓHᵧ will exchange a hydrogen atom for a fluorine atom before reacting with a bare tungsten site. Once all fluorine content is removed, silane dissociates readily on reduced tungsten sites to produce hydrogen-terminated (Wₙ(-H)) and silicon subhydride-terminated (Wₙ(-SiHₓ)) sites. For inadequate exposure of silane, hydrogen-terminated sites will remain at the end of the cycle dose, [155, 156] while at higher concentrations, H atoms, being the more weakly bound species, will be displaced by silicon subhydrides. Sault and Goodman conclude in their study of silicon-modified W(110) surfaces that reduction of WF₆ is more favorable when a monolayer of silicon coverage is present on the tungsten surface. [194] Therefore, we can conclude that a strong correlation exists between silane pressure and conformality.

3.5.3 Reaction of WF₆ on coalesced, SiHₓ-terminated W(110)

During subsequent does of WF₆, previously deposited W is passivated by silicon hydride (Wₙ(-SiHₓ)) species. Upon exposure to WF₆, terminal silicon hydride groups strip fluorine atoms from WF₆ and etch from the surface as volatile SiFₓHᵧ species. [85] At lower temperatures (less than 600K), experimental evidence shows that all silicon is stripped from the surface [72] and films are fluorine-free. Therefore, we can conclude that etching of the surface, via WF₆ reduction, leaves reactive W sites available for deposition and that there is a simultaneous etching of SiFₓ and depositing of W, resulting in a non-equilibrated state of the surface, which is a driving factor in this half-cycle.
If tungsten surface sites are passivated with hydrogen versus silicon subhydrides, as discussed in the previous section, the site will be less reactive since it is hydrogen is a weaker reductant. For this reason, an adequate exposure of silane is necessary to displace adsorbed hydrogen atoms. [156]

3.5.4 Self-Limiting Nature of ALD Half-Cycles

Initial Tungsten Dose

For a true ALD process, doses of WF$_6$ and SiH$_4$ should be inherently self-limiting. During the tungsten dose, the self-limiting nature has been attributed to 1) formation of a two-dimensional network of chemisorbed tungsten fluorides, which blocks further reduction of WF$_6$ [62, 98] and 2) sealing of the Si substrate from WF$_6$ by coalesced W. However, the latter explanation does not account for the highly porous films (density of 75% bulk value) [53] and the ability of silicon atoms to penetrate through metallic tungsten. [72, 142, 141, 173] Therefore, reduction of WF$_6$ by Si(100) silicon atoms would be possible until the tungsten film was coalesced. The density of the nuclei in the W ALD film is shown in the SEM image in Figure 11. [97]

Our DFT results support the formation of the two-dimensional network of tungsten sub-fluorides. Specifically, we find that adsorbed tungsten subfluorides undergo a conformational change so that fluorine atoms are close to being on the same plane (Figures 3.10 and 3.12). This planar conformation of fluorine atoms creates a network between neighboring sites and can lead to polymerization into a two-dimensional network on the substrate surface blocking further reduction of WF$_6$ by the silicon surface. Deposition in sequential doses is highly dependent on removal of fluorine ligands by the reductant, in this case, silane. This conclusion is in agreement with the experimental observation that
smaller reductant exposures lead to less silicon uptake and therefore less W deposition in successive WF$_6$ half-cycles. [97]
As further support, Lifshitz and Green studied similarities between Mo and W deposition on silicon and found that two key differences exist: 1) W deposition had a self-limiting nature whereas Mo had continuous growth; and 2) the fluorine concentration in the W films was an order of magnitude larger than in Mo. From these findings, they suggested that the self-limiting reaction was due to the presence of fluorine-containing intermediates. However, it should be noted that with adequate concentrations of SiH₄, W films will be fluorine-free. [98]

Silane Dose

The self-limiting nature of the SiH₄ half-cycle is attributed to silicon-hydride saturation of the W surface following the removal of terminal fluorine as SiFₓHᵧ. Support for this conclusion is drawn from the experimental finding that as silicon coverage increases on a W(110) surface, the probability of silane dissociation remains greater than 0.5 until a monolayer of silicon is deposited. Once the first monolayer is complete, the probability of silane dissociation decreases sharply to less than 0.0135. Therefore, the reaction is limited by availability of tungsten sites, which become inactive after adsorption of silicon-hydrides.

3.6 Summary and Conclusions

In this paper, we present a detailed analysis of reaction mechanisms that lead to nucleation during the deposition process of tungsten on Si(100) and W(110). Results from this study support the experimental observation that when the system is below the ALD temperature window, the system cannot overcome the energy barriers associated with WF₆ chemisorption and is therefore limited to physical adsorption. Interactions change signifi-
cantly once the exposure temperature is sufficiently high enough to sample chemisorption pathways. During the WF$_6$ dose, WF$_6$ interacts with silicon surface sites with a ratio of 1:2 to produce chemisorbed WF$_x$H$_y$. This ratio would result in incomplete coverage on the surface. However, removal of stable Si-F$_{(s)}$ sites through SiF$_x$H$_y$ etching creates availability on the surface for additional deposition. Conformal coverage of tungsten during the first dose therefore depends on etching of fluorine-stabilized silicon sites. However, partial W coverage is supported during early cycles since adsorbed WF$_x$ species would act as steric inhibitors to etching and deposition as the cycle proceeds. Therefore, until the film has coalesced, the Si(100) surface acts as a reducing agent in early cycles of WF$_6$.

In the sequential half-cycle, SiH$_4$ plays the essential role of extracting fluorine atoms from the newly formed W layer. Additional deposition is dependent on the reduction of chemisorbed WF$_x$ since WF$_6$ cannot adsorb onto WF$_x$. Once all the fluorine is removed, additional SiH$_4$ molecules dissociate on bare surface sites to generate a monolayer of silicon-hydrides. The self-limiting nature is attributed to silicon-hydride saturation on the W surface. An inadequate concentration of SiH$_4$ would result in hydrogen-passivated sites, which would lessen the concentration of SiH$_x$ sites, which act as reducing agents in consecutive doses. Once a conformal film has been deposited, WF$_6$ interacts with a layer of silicon-hydrides on W(110), which act as the reductants of WF$_6$ and are removed as volatile SiF$_x$H$_y$ species. Conversion of surface silicon-hydrides to silicon-subfluorides, with WF$_6$ acting as the fluorine-donor, is an essential step for the silicon-hydride monolayer to etch from the surface as a volatile, gas-phase species. Thermodynamically favorable removal of this monolayer reinforces the experimental observation that the W-ALD films contain no measurable concentration of fluorine or silicon. The self-limiting nature of later half-cycles of WF$_6$ is attributed to the complete removal of silicon-hydrides from the surface since these species act as the reductants of WF$_6$. Based on the energetics
and experimental evidence, WF$_x$H$_y$, SiF$_x$, and H$_2$ molecules are released during the ALD process. Strong surface attractions calculated for tungsten subfluorides, e.g. WF$_3$H and WF$_4$H$_2$, support the absence of these species in experimental gas-phase analysis. Conclusions drawn from this data can be extended to study selective deposition on silicon and silica. [53, 97, 81, 81] By-products that may contribute to nucleation on the non-selective surfaces are WF$_a$H$_b$, SiF$_x$H$_y$, and H$_2$.

### 3.7 Acknowledgement

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### 3.8 Future Directions

For our theoretical study, Density Functional Theory (DFT) is being used to perform electronic structure calculations for the common SiH$_4$/WF$_6$ tungsten ALD. During this process, selective tungsten nucleation proceeds on Si relative to SiO$_2$. However, there are several available reaction pathways that allow for nucleation on SiO$_2$, which limits the W ALD selectivity window. The results in this paper demonstrate that we are capable of calculating the energy barrier for a reaction that, under the right conditions, would lead to unwanted nucleation. This process, once optimized, will be extended to more complex systems and will allow for us to quantify the reaction energetics, which will be implemented into a reactive force field to simulate the time evolution of the systems. At the end of our study, our work will help the electronics research community better understand the fundamental limits of area-selective atomic layer deposition, by providing
firm quantifiable parameters to compare with other methods, thereby promoting the con-
tinued success of feature-scale advancement to sub-10 nm nodes. The succeeding chapter
provides an in depth look into the reactions that govern two area-selective atomic layer
deposition (AS-ALD) processes.
Chapter 4

Ab Initio Study of Nucleation Energetics during Initial Exposure of TiCl$_4$, H$_2$O, WF$_6$ and SiH$_4$ on Si and SiO$_2$ Substrates during Area-Selective Atomic Layer Deposition of TiO$_2$ and W

Mariah J. King, Patrick Theofanis, Paul C. Lemaire, Erik E. Santiso and Gregory N. Parsons$^a$
4.1 Abstract

We present nucleation kinetics of WF\textsubscript{6}, TiCl\textsubscript{4}, SiH\textsubscript{4}, and H\textsubscript{2}O on Si(100)-H and/or SiO\textsubscript{2} substrates during Area-Selective Atomic Layer Deposition of TiO\textsubscript{2} and W, while considering different types of hydroxyl groups present on the oxide. From the DFT calculations we have proposed nucleation schemes that support native selectivity between substrates as well as those that may lead to non-selective growth during W and TiO\textsubscript{2} AS-ALD processes. Furthermore, the presented results reveal a novel approach for determining surface site selectivity during ALD processes for various precursor chemistries. Insight from this work helps expand understanding of inherent substrate selective ALD, where native differences in substrate surface reaction chemistry are used to promote desired selective-area growth.

4.2 Introduction

Area Selective Deposition (ASD) relies on chemical reactivity to deposit material on specific growth areas in a selective manner. Using selective chemical processes versus photolithography and etching steps (top-down techniques) as a method for self-alignment and patterning enables a cost-effective option for bottom-up device fabrication. Hence, there is significant interest in developing and implementing area-selective fabrication schemes. Atomic layer deposition (ALD) is a layer-by-layer growth technique that is shown to promote atomic-scale precision of thickness, composition and conformatility. Deposition is achieved through alternating exposures of various vapor-phase precursors that undergo self-limiting surface reactions with a substrate. ALD of materials such as metals, [163, 94, 121, 6, 39] metal oxides, [174, 175, 74, 23] and metal nitrides [151, 181,
have been successfully demonstrated on a single substrate. However, area selective ALD (AS-ALD) on a desired growth area versus an undesired-growth surface is only feasible as long as the substrate chemistry and by-products are controllable throughout the process and do not interfere with selectivity. Advancements in AS-ALD processes are reliant on in-depth studies that explore the underlying mechanisms that drive deposition on the growth area (GA) and non-growth area (NGA).

The goal of AS-ALD is to deposit thin films at specific location on a pre-patterned heterogeneous surface. The surface can consist of different materials or the same material with different surface groups patterned atop. The aim is to deposit a desired material only on the GA, while preventing deposition from occurring on the NGA. This is accomplished by the chemical alterations on the surface that promote favorable (fast, or energetically exothermic) or unfavorable (slow, or energetically endothermic) surface reactions so that nucleation on the NGA is inhibited for as long as possible. The ideal AS-ALD process would delay nucleation on the NGA indefinitely and, therefore, would only show growth on the GA. The favored interaction between the precursor and the GA leads to efficient deposition and no deposition or a sufficient nucleation delay that allows for desired film thickness. (Example, WF$_6$ on Si (GA) and SiO$_2$ (NGA) leads to linear growth on the GA while negligible growth is observed on NGA). A key principle in developing a successful area-selective process is optimizing the thermodynamic difference between the growth mechanism on the GA the NGA. [108]

For an AS-ALD process, the heterogeneous surface is exposed to a deposition precursor and a co-reactant. A key factor is guaranteeing that chemoselectivity is upheld by both reactive components. However, even though one reactant may show chemoselectivity towards the GA and NGA surface, if the other reactant alters the NGA surface chemistry through a side-reaction (e.g. oxidation, reduction, chemisorption), then non-
selective deposition may be initiated. Reactivity of precursors towards surface groups will ultimately determine whether AS-ALD can be achieved for a given system and can be explored in-depth using ab initio techniques. [107]

4.3 Simulation Methods

The structures and associated adsorption energies were calculated for precursors and co-reactants for two AS-ALD materials and surfaces of current interest. Specifically, we examined: 1) energetics of the reactants for tungsten AS-ALD (i.e. WF$_6$, and SiH$_4$) interacting with the GA (hydrogen-terminated Si(100) and the NGA (SiO$_2$ with 5.07 OH/nm$^2$ and 3.38 OH/nm$^2$); and 2) energetics of TiO$_2$ AS-ALD (i.e. using TiCl$_4$ and H$_2$O) interacting with the GA (SiO$_2$ with 5.07 OH/nm$^2$ and 3.38 OH/nm$^2$) and the
NGA (hydrogen-terminated Si(100)). Electronic structure calculations were performed using the projector-augmented wave function as implemented in Vienna Ab Initio Simulation Package (VASP). Calculations were carried out using the generalized gradient approximation to the density functional theory (DFT). Perdew-Berke-Ernzerhof (PBE) exchange-correlation functionals were employed. Additional computational details can be found Chapter 3 and system preparation scripts used to generate data can be found in the Appendix B.

Interaction energies were calculated for the surface interactions using the general equation shown below:

\[ \Delta E_{0,\text{Interaction}} = [E_{0,\text{Slab}} + E_{0,\text{Precursor}}] - [E_{0,\text{Slab+Adsorbant}} + E_{0,\text{by-products}}] \quad (4.1) \]

The energy calculated using Equation 1 provides information on the reaction energetics at 0K and do not include information on the enthalpy or entropy. The reaction barrier, calculated for select reactions using the zero temperature string method [32, 138] provides information on the nucleation kinetics. For chemical systems within the same family, the reaction barrier heights scale with reaction energy. [37, 58] Therefore, it is unlikely to have an endothermic reaction with a low barrier when comparing to a similar exothermic reaction with a high barrier.

### 4.4 Surface Chemistry

Details on the system preparation of Si(100)-H are provided in Chapter 3, section 3.3.1.

The silica slab was modeled using two geometries of amorphous SiO\(_2\) with different
surface hydroxyl concentrations (3.38 OH/nm$^2$ and 5.07 OH/nm$^2$) provided by Sandupatla et al. [152] Further information on the silica slabs construction can be found in the referenced paper.

Three kinds of OH groups can exist on the surface of oxides: isolated, vicinal and geminal. Bridging oxygen’s can also act as reactive sites for ALD and CVD at higher temperatures. The concentration of each type of hydroxyl is dependent on surface preparation and system temperature. Vicinal and geminal groups are dominant at low temperatures but are condensed at higher temperatures by dehydroxylation to form oxygen bridges. At low temperatures, the hydroxyl groups mainly play the role of adsorption sites. Additional information on hydroxyl group chemistry can be found in a comprehensive review article written by L.T. Zhuravlev. [196, 86]

![Figure 4.2: Schematic illustration of hydroxyl group types: isolated (left), vicinal (middle), geminal (right) and bridged surface oxygen.](image)

The average hydroxyl group density is 4.9 ±1 OH/nm$^2$ out of a total of 8 sites/nm$^2$. [196] In this study we used silica surfaces with 3.38 OH/nm$^2$ coverage and 5.07 OH/nm$^2$ coverage as depicted in Figure 4.3.
4.5 Precursor Chemistries

4.5.1 $\text{WF}_6/\text{SiH}_4$

$\text{WF}_6$ is a common ALD/CVD precursor used for thin film tungsten deposition. It has a molecular weight of 297 g/mol and a low electron affinity due to extra electron localization on the tungsten atom and the highest occupied molecular orbital being delocalized over the fluorine atoms, which results in a very high ionization potential. [119] $\text{WF}_6$ has a low electron affinity since the 4d orbital is adequately filled due to the electron contribution from the fluorine ligands.

$\text{SiH}_4$ is an W ALD/CVD co-reactant used as a reducing agent in W-ALD. It has a molecular weight of 32.12 g/mol and is known for its hydridic behaviour. The silicon atom is less electronegative than hydrogen, as a result, the silicon-hydrogen bond is weaker than that of hydrogen gas (another common reducing agent in ALD/CVD) with a value of 316 kJ/mol versus 432 kJ/mol.

4.6 $\text{TiCl}_4/\text{H}_2\text{O}$

$\text{TiCl}_4$ is a common $\text{TiO}_2$ ALD/CVD precursor used for thin film deposition of $\text{TiO}_2$ and TiN. It has a molecular weight of 186.79 g/mol and contains an empty orbital that is capable of accepting an electron pair (Lewis acid) in the ALD process and is known for its oxophilicity, or tendency to form oxides by hydrolysis or abstraction of oxygen. $\text{TiCl}_4$ has a higher electron affinity than tungsten since the four outer electrons are donated to fill the 3p orbitals of the chlorine ligands making titanium electron deficient. [187]
4.7 Results

DFT calculations were performed to better understand mechanisms that govern chemoselective adsorption of WF$_6$, SiH$_4$, TiCl$_4$ and H$_2$O on silicon (100) and two silica surfaces with differing surface hydroxyl density. Crystalline Si(100) and amorphous SiO$_2$ (5.07 OH/nm$^2$ and 3.38 OH/nm$^2$) are representative of experimentally used surfaces. For the SiO$_2$ surface, calculations reveal that physical interactions are stronger at sites with electron deficient oxygen atoms and become stronger in order of H$_2$O, WF$_6$, TiCl$_4$, SiH$_4$. Chemisorption energetics on SiO$_2$ is dependent on hydroxyl type with the isolated group being the most favorable in order of SiH$_4$, TiCl$_4$, WF$_6$. On the Si(100)-H surface, favorability of chemisorption is also in order of H$_2$O, SiH$_4$, TiCl$_4$, WF$_6$.

4.7.1 Physical Adsorption of Reactants on SiO$_2$ surface with 5.07 and 3.38 OH/nm$^2$

Physical adsorption is the first step in precursor nucleation. On SiO$_2$, different forms of surface hydroxyl groups exist and, hence, the energy associated with physisorption will vary across the surface and between surfaces with different hydroxyl concentration. The changes in energy that occur between separated reactants and physisorbed states (Equation 4.1) on the SiO$_2$-OH surfaces were identified by DFT calculations and are depicted in Figure 4.4 for H$_2$O (left), WF$_6$ (middle-left), TiCl$_4$ (middle-right) and SiH$_4$ (right) for 5.07 OH/nm$^2$ (top) and 3.38 OH/nm$^2$ (bottom). As evident from Figure 4.4, the precursors exhibit distinct reactivity towards different hydroxyl group chemistry.

On the 3.38 OH/nm$^2$ surface, the closest hydroxyl group distance 2.94Å, whereas on the 5.07 OH/nm$^2$ surface, the closest is 1.86Å. To dissect the information in Figure 4.4, we use a top vs. bottom approach to compare 3.38 OH/nm$^2$ versus 5.07 OH/nm$^2$ and a
Figure 4.3: Minimum energy structure of top 3A of SiO$_2$ surface with 5.07 OH/nm$^2$ (left) and 3.38 OH/nm$^2$. Isolated hydroxyl groups are labeled as i, vicinal hydroxyl groups are labeled as v and geminal are labeled as g. Vicinal groups are defined by neighboring, hydrogen bonded hydroxyl groups; the group that is sharing a proton is labeled with a and the group accepting a proton is labeled with b (i.e. v1a is a vicinal hydroxyl group that is sharing a proton with v1b).

right to left approach to compare precursor chemistry.

3.38 OH/nm$^2$ vs 5.07 OH/nm$^2$: For the top vs. bottom approach, the top right of each box corresponds to physisorption at a vicinal site (v1b). The O atom of v1b is 2.94Å from the hydrogen on v1a on the 3.38 OH/nm$^2$ surface and 2.04Å away on the 5.07 OH/nm$^2$ surface. Since v1a, the co-vicinal group, is sharing a proton with v1b, v1b can undergo an exchange reaction more easily on the 5.07 surface; depicted by the darker color boxes on top versus bottom. On the other hand, the v1a (top left), the proton donating group is more likely to undergo an exchange reaction on the 3.38 OH/nm$^2$ surface (depicted by the lighter color boxes on top versus bottom). Isolated group, i3, is present on both
Figure 4.4: DFT (GGA/PBE) minimum energy mapping data for the physical adsorption (physisorption) of WF$_6$ (left), TiCl$_4$ (middle) and SiH$_4$ (right) on SiO$_2$ surface with 5.07 OH/nm$^2$ (top) and 3.38 OH/nm$^2$ (bottom).

3.38 OH/nm$^2$ and 5.07 OH/nm$^2$. On both surfaces, this group has a lower z value than all other hydroxyl groups, making it less accessible to gaseous molecules. Therefore, the physical interaction is weak and only slightly more favorable on the 5.07 OH/nm$^2$ surface, on which i3 appears to be slightly raised.

Geminal groups are unique to the 5.07 OH/nm$^2$ surface. For the most part, physisorption at the g2 site, which has a more upright orientation than g1, is energetically more favorable. Altogether, Figure 4.4 depicts that gaseous molecules interacts more strongly if the oxygen atom is accessible and electron deficient.

WF$_6$/SiH$_4$ and TiCl$_4$/H$_2$O: Between WF$_6$ and SiH$_4$, the physical interactions of WF$_6$ is stronger than that of SiH$_4$ on the 3.38 and 5.07 OH/nm$^2$ surface. The interaction of SiH$_4$ on both surfaces is predominantly neutral. For TiCl$_4$ and H$_2$O, the physical interaction of H$_2$O is stronger than that of TiCl$_4$ at most hydroxyl sites. Additionally, in comparison of all four reactants, H$_2$O exhibits an endothermic physical interaction at
the most surface sites.

4.8 Chemical Adsorption on SiO$_2$ surface with 5.07 and 3.38 OH/nm$^2$

In order to investigate precursor adsorption on the different hydroxyl groups, DFT was used to calculate the overall energy change for WF$_6$, TiCl$_4$, and SiH$_4$ chemisorbing onto isolated, vicinal and geminal hydroxyl groups. H$_2$O can undergo reaction with bridging Si-O-Si groups on SiO$_2$ but this reaction was not investigated here.

Figure 4.5: DFT (GGA/PBE) minimum energy calculations for adsorption of WF$_6$ (left), TiCl$_4$ (middle) and SiH$_4$ (right) at a isolated hydroxyl site (left), geminal hydroxyl site (right) and vicinal hydroxyl site (right). Reactants (top) correspond to separated gas phase precursor and SiO$_2$ surfaces and are taken as reference points to calculate $\Delta E$.

WF$_6$: Chemisorption at the geminal hydroxyl group is calculated for site g2 and involves an intermediate physisorbed state that is slightly exothermic (-0.08eV). This
process is an energetically uphill path that yields HF. The overall chemisorption reaction is endothermic and requires +0.19eV. Chemisorption at a vicinal hydroxyl group is calculated for sites v1a, v1b and v2a on the 5.07 surface. Site v1a requires +0.19eV to undergo a chemisorption reaction, site v1b requires +0.08eV to undergo a chemisorption reaction and site v2a requires +0.17eV to undergo a chemisorption reaction. Chemisorption at the isolated hydroxyl group is calculated for site i1 on the 3.38 surface and involves an intermediate physisorbed state that is slightly exothermic (-0.12eV) with a slightly endothermic chemisorption reaction that requires +0.02eV.

TiCl₄: Chemisorption of TiCl₄ on the geminal hydroxyl groups is calculated for site g1 and g2. To undergo a chemisorption reaction, TiCl₄ on site g1 requires +0.24eV and on g2 requires +0.16eV with both yielding HCl. Chemisorption at the vicinal hydroxyl group is calculated for site v2a on the 5.07 surface and involves an intermediate physisorbed state that is slightly endothermic (+0.03eV) with an endothermic chemisorption reaction that requires +0.31eV. Chemisorption at the isolated hydroxyl group, calculated for site i1 on the 3.38 surface, involves an intermediate physisorbed state that is slightly exothermic (-0.02eV) and requires -0.03eV to undergo a chemisorption reaction to yield HCl.

SiH₄: Chemisorption at the geminal hydroxyl group, calculated for site g2 on the 5.07 surface, involves an intermediate physisorbed state that is slightly exothermic (-0.01eV) and requires -0.53eV for a chemisorption reaction that yields H₂. Chemisorption at the vicinal hydroxyl group, calculated for site v2a on the 5.07 surface, involves an intermediate physisorbed state that is slightly exothermic (-0.03eV) and requires -0.55eV to undergo a chemisorption reaction. Chemisorption at the isolated hydroxyl group, i1 on the 3.38 surface, involves an intermediate physisorbed state that is slightly exothermic (-0.02eV) and requires -0.71eV to undergo a chemisorption reaction.

Overall, thermodynamic favorability of chemisorption for geminal and vicinal units
on the 5.07 surface follows the order: SiH₄, TiCl₄, WF₆. For isolated units on the 3.38 surface, favorability follows the order: WF₆, SiH₄, TiCl₄. A key element is the shift in physical interaction strength when switching from the 5.07 to 3.38 surface. The physical interaction strength for hydroxyl groups follows the order isolated, geminal vicinal.

Chemical Adsorption on Si(100)-H surface: A similar analysis was performed to determine the overall energy change upon chemisorption of WF₆, TiCl₄, SiH₄ and H₂O on the H-terminated Si(100) surface. Two elementary reactions are available to these systems: direct adsorption reactions and a ligand exchange reaction; as depicted in Figure 4.6.

As shown in Figure 4.6, WF₆ can undergo a ligand exchange reaction through an exothermic process ($\Delta E = -0.65$) that involves the formation of WF₅H and a surface Si-F bond or a chemisorption reaction through an endothermic process ($\Delta E = +1.21$) that yields HF. TiCl₄ can undergo a ligand exchange reaction through an endothermic
process ($\Delta E = +0.32$) that involves the formation of TiCl$_3$H and a surface Si-Cl bond or a chemisorption reaction through an endothermic process ($\Delta E = +0.59$) that yields HCl. SiH$_4$ will undergo a chemisorption reaction through an exothermic process ($\Delta E = -0.25$eV) that yields H$_2$. H$_2$O will undergo a chemisorption reaction on Si(100)-H through an exothermic process ($\Delta E = -0.54$eV) that yields H$_2$.

For the Si(100) surface, chemisorption favorability follows the order: H$_2$O, SiH$_4$, TiCl$_4$, WF$_6$; and the exchange reaction follows the order: WF$_6$, TiCl$_4$.

### 4.9 Chemoselectivity during AS-ALD Processes

Chemoselective adsorption of the precursors on two starting surfaces can be analyzed using the results in Figures 4.5 and 4.6. Here we discuss the chemoselectivity in light of two AS-ALD processes: W ALD using WF$_6$ and SiH$_4$ and TiO$_2$ ALD using TiCl$_4$ and H$_2$O.

#### 4.9.1 Area-Selective ALD of WF$_6$/SiH$_4$

As expected from experimental observation, DFT results show that WF$_6$ is more likely to interact on Si(100) than SiO$_2$. [80, 97, 191, 82] Area-selective W-ALD (AS-WALD) is founded on this principle and has been demonstrated using WF$_6$ and SiH$_4$ as co-reactants. The SiO$_2$ behaves as the NGA since oxidized silicon atoms are less likely to act as sacrificial reductants. [26] However, experiments show that deposition occurs on the NGA after a 30-35 cycle delay at 220°C. The appearance of W nuclei on SiO$_2$ has been attributed to SiO$_2$ surface modification via reaction with SiH$_4$, WF$_6$, or WF$_6$ by-products, such as WF$_4$. The delay is ascribed to the difference in kinetic and thermodynamic favorability towards the NGA versus GA surface, with the thermodynamic difference determined from
the DFT calculations to be (-0.90eV on SiH\textsubscript{4} vs. SiO\textsubscript{2}). SiH\textsubscript{4} is more likely to interact with SiO\textsubscript{2} than Si(100) indicating that the more likely pathway for loss of selectivity is SiH\textsubscript{4} adsorption on SiO\textsubscript{2} (-1.0eV on SiO\textsubscript{2} vs. Si(100)). Loss of selectivity has been proposed to be caused by a buildup of silicon hydrides on the silica surface. The highly exothermic reaction energetics derived from DFT calculations provide support for the nucleation of silicon islands on silica that promote tungsten deposition.\cite{55, 189} Figure 4.7 depicts the scheme for loss of selectivity during the AS-WALD process. In addition, Groenen \textit{et al.} conducted a study on selectivity loss during W CVD and concluded that pre-exposure to SiH\textsubscript{4} resulted in a drastic decrease in the time required to reach an amount of W deposited on SiO\textsubscript{2} and that during pre-exposure an increased H\textsubscript{2} signal was observed, possibly indicating a reaction of SiH\textsubscript{4} molecules in the reactor.\cite{55} Based on our calculations, the increase in H\textsubscript{2} signal during SiH\textsubscript{4} exposure on SiO\textsubscript{2} is due to an exothermic chemisorption of SiH\textsubscript{3}.

Chemisorption of W onto Si(100) occurs follows the reduction of WF\textsubscript{6} through the exothermic ligand exchange reaction with surface silicon sites. The mechanism for WF\textsubscript{6} adsorption is discussed in detail in a previous study.\cite{82}

### 4.9.2 Area-Selective ALD of TiCl\textsubscript{4}/H\textsubscript{2}O

Experimentally, when SiO\textsubscript{2} and Si(100) are exposed simultaneously to TiCl\textsubscript{4}, nucleation is observed on SiO\textsubscript{2} without delay as opposed to Si(100)-H on which a nucleation delay is measured. Overall, the TiCl\textsubscript{4}/H\textsubscript{2}O AS-ALD process has demonstrated less than 2 nm of incomplete selective deposition on SiO\textsubscript{2} with many nuclei on the Si(100) surface. The nucleation difference observed on the two surfaces TiO\textsubscript{2} can be explained by the reaction energetics, which show that TiCl\textsubscript{4} requires -0.02eV to chemisorb on SiO\textsubscript{2} while
Figure 4.7: Schematic illustrating a surface modification of SiO$_2$ through SiH$_4$ adsorption that promotes tungsten nucleation during area-selective W ALD that leads to loss of selectivity.

requiring +0.59 eV to chemisorb on Si(100). However, it has been shown experimentally that exposure of silicon to TiCl$_4$ results in etching of the silicon surface through a TiCl$_4$ reduction reaction that leads to Ti deposition. [44] The DFT calculations show that the reduction reaction between Si(100) and TiCl$_4$ is the more probable route (+0.28eV) for deposition. DFT calculations performed by Hu et al. and McDonnell et al. support these findings. [68, 113] Therefore, poor selectivity of TiCl$_4$ towards SiO$_2$ and Si(100) is due to the small energy difference between the chemisorption reaction with SiO$_2$ and the reduction reaction with Si(100); TiCl$_4$ is only -0.3eV more likely to interact on SiO$_2$ versus SiH. Based on the DFT results, favored growth on SiO$_2$ is attributed to an interaction with isolated surface hydroxyls indicating that selectivity will be enhanced at higher temperatures or by surface preparation techniques that promote dehydroxylation. [169, 96]

During the TiO$_2$ AS-ALD process, H$_2$O plays the essential role of hydrolyzing chemisorbed TiCl$_4$ in preparation for the succeeding dose of TiCl$_4$. However, H$_2$O can also favorably undergo hydrolysis on the Si(100)-H surface, altering the surface chemistry of the NGA; thus, promoting TiCl$_4$ nucleation and non-selective growth. Therefore, there exists two
pathways by which non-selective growth could occur, one being nucleation of TiCl$_4$ on the Si(100) surface and the other being oxidation of hydrogen-terminated Si(100) via water exposure. In a study of TiO$_2$ AS-ALD by Atanasov et al., the authors concluded that eliminating water delays the oxidation of the hydrogen-terminated silicon, thereby impeding TiO$_2$ film growth. [2]

4.10 Conclusions

We have presented nucleation kinetics of WF$_6$, TiCl$_4$, SiH$_4$, and H$_2$O on Si(100)-H and/or SiO$_2$ substrates during Area-Selective Atomic Layer Deposition of TiO$_2$ and W, while considering different types of hydroxyl groups present on the oxide. From the DFT calculations we have proposed nucleation schemes that support native selectivity between substrates as well as those that may lead to non-selective growth during W and TiO$_2$ AS-ALD processes. Furthermore, the presented results reveal a novel approach for determining surface site selectivity during ALD processes for various precursor chemistries. Insight from this work helps expand understanding of inherent substrate selective ALD, where native differences in substrate surface reaction chemistry are used to promote desired selective-area growth.

4.11 Supplemental Methods

A python script was used to generate the physisorption maps shown in Figure 4.4. The code along with example geometry files are included in Appendix B.
4.12 Acknowledgments

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Chapter 5

Coarse-Grained Molecular Dynamics Study of Ethoxylated Surfactant–Mediated Vapor-Liquid Interface of Water: Effect of Molecular Architecture

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5.1 Abstract

We present results from coarse-grained molecular dynamics simulations illustrating the relationship between the tail group topology of a class of nonionic surfactants, alcohol ethoxylates (AE’s) and their ability to lower the surface tension at the water vapor-liquid
interface. We find that branching of AE surfactants allows for a range of water vapor-liquid surface tension values ranging from 10 mJ/m$^2$ to 65 mJ/m$^2$. Our results indicate that branch location and head to tail bead ratio significantly impact a surfactant’s ability to lower the surface tension at the vapor-liquid interface of water. Furthermore, the more effective surfactant topologies enable a strong tail-tail interaction without interfering with the head-water interaction. For example, a branch that is constricted adjacent to the head group (cross-shaped) has a negative effect of reducing the interaction between the head group and water because of the repulsive interaction between the branch and water. Furthermore, surfactants that effectively reduce surface tension have an effect of widening the interfacial region. Conclusions drawn from this study can be applied to surfactant design in the effort to replace perfluorinated surfactants. The method used to obtain these results is also a first step toward the development of a predictive model connecting the topology of surfactants with interfacial tension.

5.2 Introduction

Ethoxylated fatty acids and alcohols (AE) are known from decades of application to be excellent surfactants. [157] Their surface properties at the water vapor-liquid interface have been extensively studied along with their environmental and human risk factor. The overall consensus is that this major class of non-ionic surfactants is safe and effective for household and industrial applications. [60] Branched alcohol ethoxylates, a subgroup of ethoxylated surfactants, remain in discussion due to controversial or inconclusive evidence. [42] For instance, a risk assessment performed by the Environmental Protection Agency (EPA) concluded that branched AE’s are not more toxic than linear AE’s with the same number of carbon atoms in the hydrocarbon chain, [60] while another study by
Kravetz and coworkers concluded that surfactants with more than one internal methyl branch per hydrophobe biodegrade slower than their linear counterparts. [161, 88] Moreover, branched surfactants, such as the Guerbet type (T-shaped), [185] are shown to have good environmental properties, including lower aquatic toxicity and easy biodegradation.

Knowledge of branched AE’s is far less extensive than that of linear AE’s due to the widespread application and efficiency of linear-based hydrophobes. The level of controversy surrounding branched alcohol ethoxylates, along with their potential to replace perfluorinated surfactants, warrants further investigation. [117, 116] Replacing perfluorinated surfactants in Teflon manufacturing, CO₂-based applications, etc. with branched AE’s is a highly desirable prospect since perfluorinated compounds are becoming notorious for extreme environmental persistence to biodegradation due to their high stability. [45]

Using the summary of a large amount of thermodynamic and experimental data, [184, 14] widely applicable and acceptable quantitative structure-property relationship (QSPR) models have been established between surfactant structures and physiochemical properties. [66] However, detailed studies that further understanding of surface interactions are less accessible. Therefore, given the potential replacement of branched AEs for perfluorinated surfactants, a fundamental understanding of branching effects on interfacial tension is essential for rapid replacement of equal applicability.

The goal of the current project is to provide an in-depth understanding of how variations in AE branching effect performance, while also establishing a method for studying a large set of branched and linear AEs. To gain a thorough understanding of AE branching, 100+ surfactants, including linear hydrophobes, were investigated at the water vapor-liquid interface using coarse-grained molecular dynamics. We present results depicting the relationship between surface tension and branch location, branch density,
branch length and head group length.

Our results show that branching of surfactants allows for a larger range of critical surface adsorption ($\Gamma_{Max}$) values and surface tension ($\gamma$) values while using a constant number of head and tail beads. Results from the topology analysis suggest that the more effective surfactants (i.e., those that achieve a larger reduction in the surface tension) include branching that is not neighboring the tail-adjacent head bead and that increase tail–tail interaction without significantly increasing the length of the tail group. Furthermore, an optimal relationship is seen to exist between the branch length, linear tail length (or backbone) and head group length. If the tail–tail interaction is too strong, the head–water interaction decreases and results in less effective surfactants. In addition to the qualitative results, we present the computational technique used to develop the database of linear and branched surfactants, which can be used for further examination of surfactants. Overall, we present a new technical process and fundamental results that can be used to guide experimental efforts in designing new surfactants.

5.3 Methods

Coarse-grained (CG) models provide an efficient means to investigate complex systems that are inaccessible to fully atomistic representations, such as a surfactant–water system. [170] The reduced number of degrees of freedom and softer potentials associated with lumping of atoms into coarse-grained beads allow for larger simulation sizes and longer time-scales. The coarse-grained model for the surfactant–water system was developed by Lobanova et al. [5, 4, 95, 131, 102, 104] using the group contribution statistical associating fluid theory (SAFT-$\gamma$). [5, 4, 95, 122] This method uses a top-down approach, in which a molecular-based equation of state is used to obtain an intermolecular potential
that reproduces experimental thermophysical properties over a wide range of conditions. A top-down methodology offers the advantage of greatly reducing the computational burden usually associated with the determination of accurate intermolecular parameters. Additionally, the flexibility of the Mie-based SAFT-$\gamma$ force fields enables one to explore widely differing forms of intermolecular potentials by varying the hardness/softness of the repulsion and the range of attraction between segments. \[55\] The SAFT-$\gamma$ force field successfully reproduces experimental data for water, greenhouse gases, long alkanes and hetero-group molecules. \[5, 4, 95, 22, 171\]

The interactions of the coarse grained beads were modeled using the Mie potential. \[115\] This potential is a general form of the Lennard-Jones potential, meaning that the exponents are independently adjustable from the Lennard-Jones epsilon and sigma parameters, allowing extra degrees of freedom to fit a wider variety of coarse-grained chemistries. The two exponents $\lambda_r$ and $\lambda_a$ characterize the softness/hardness of the repulsion and the range of the attraction, respectively. In the Lennard-Jones potential, the most common values of $\lambda_r$ and $\lambda_a$ are 12 and 6, respectively. The expressions for the Mie potential are given by Equation 5.1 and Equation 5.2.

$$\mathcal{U}^{\text{Mie}(r)} = C\epsilon \left[ \left( \frac{\sigma}{r} \right)^{\lambda_r} - \left( \frac{\sigma}{r} \right)^{\lambda_a} \right]$$  \hspace{1cm} (5.1)

$$C = \frac{\lambda_r}{\lambda_r - \lambda_a} \left( \frac{\lambda_r}{\lambda_a} \right)^{\frac{\lambda_a - \lambda_r}{\lambda_r - \lambda_a}}$$  \hspace{1cm} (5.2)

where $\epsilon$ is the potential well depth, $\sigma$ is the segment diameter, $r$ is the inter-segment distance, and the constant $C$ is defined to ensure that the minimum of the potential well is $-\epsilon$. The two exponents $\lambda_r$ and $\lambda_a$ characterize the softness/hardness of the repulsion and the range of the attraction, respectively. Table 5.1 shows the parameters used to model the
water and surfactant coarse-grained beads. The water molecules were parameterized using the Mie-based SAFT-$\gamma$ methodology to reproduce experimental vapor-liquid equilibrium and surface properties for a water dimer.

Table 5.1: SAFT-$\gamma$ and Mie potential parameters for beads in the surfactant systems. Lorentz-Berthelot combining rules are used to describe unlike pair interactions.

<table>
<thead>
<tr>
<th>Bead Name</th>
<th>Sigma ($\sigma$) (Å)</th>
<th>Epsilon ($\epsilon$) (kcal/mol)</th>
<th>$\lambda_r$</th>
<th>$\lambda_\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water Dimer</td>
<td>3.75</td>
<td>399.96</td>
<td>8</td>
<td>6</td>
</tr>
<tr>
<td>Tail Bead (CM): -CH$_2$CH$_2$CH$_2$-</td>
<td>4.36</td>
<td>344.42</td>
<td>15</td>
<td>6</td>
</tr>
<tr>
<td>Head Bead (EO): -CH$_2$CH$_2$O-</td>
<td>4.06</td>
<td>396.60</td>
<td>19</td>
<td>6</td>
</tr>
<tr>
<td>Terminal Head Bead (OA): -CH$_2$OH</td>
<td>3.72</td>
<td>461.11</td>
<td>19</td>
<td>6</td>
</tr>
<tr>
<td>OA-EO</td>
<td>3.89</td>
<td>392.00</td>
<td>19</td>
<td>6</td>
</tr>
<tr>
<td>OA-W</td>
<td>3.73</td>
<td>492.00</td>
<td>11.94</td>
<td>6</td>
</tr>
<tr>
<td>EO-CM</td>
<td>4.21</td>
<td>352.00</td>
<td>16.86</td>
<td>6</td>
</tr>
<tr>
<td>EO-W</td>
<td>3.90</td>
<td>480.00</td>
<td>11.94</td>
<td>6</td>
</tr>
<tr>
<td>CM-W</td>
<td>4.05</td>
<td>250.00</td>
<td>10.85</td>
<td>6</td>
</tr>
</tbody>
</table>

System sizes were accessible to all-atom simulations; however, CG models allowed for a more efficient means to measure surface tension for larger topology spaces. The timescale to calculate surface tension via all-atom simulations are on the order of months considering our method requires 20 ns of simulation time. The novelty of this model is that a series of systems consisting of 5,000 to 10,000 coarse-grained beads, approximately 20 ns, can be completed on the order of days. In addition, the method for generating the series of configurations is programmed so that all configurations are submitted automatically and the information output requires minimal post-processing.

The objective of this project is to describe the relationship between tail group topology and physical properties; therefore, to reduce the complexity of the system, surfactants
were limited in chemical composition to three types of coarse-grained Mie segments: 1) a terminal head bead (-CH₂OH) used for data analysis and 2) an additional head-group bead (-CH₂CH₂O-) both parameterized to interact strongly with water; and 3) an alkane-like segment parameterized to reproduce properties of compounds from the alkyl series (-CH₂CH₂CH₂-). Beads were parameterized to fit experimental properties and the exact chemistry of the bead is specific to the location within the surfactant, i.e. the alkane-like segment can be represented as -CH₂- or -CH₃ as depicted in Figure 5.2. A terminal specific chemistry for the head bead (OA) is used in order to precisely determine the distance between the terminal head bead and water interface. AE surfactants are described throughout the rest of the paper using the nomenclature used by the human environmental risk assessment (HERA) [60] to be the basic structure of CₓEOₙ. Two structures of AE’s used in household cleaning products are shown below in Figure 5.1.

![Figure 5.1: Two principal structures of AE’s used in cleaning products: a linear AE (C₈EO₃, top) and a branched AE (C₈EO₃, bottom)](image-url)
5.3.1 Molecular Dynamics Simulations

All simulations were performed using the molecular dynamics program LAMMPS (Large-scale Atomistic/Molecular Massively Parallel Simulator). [140] Simulations were run at a temperature of 298.15K in the canonical (NVT) ensemble, and Newton’s equations of motion were integrated with the velocity Verlet algorithm using a Nosé-Hoover thermostat and a time step of 2.0 fs. [64, 127, 186] A time-step analysis is provided in Appendix A. The potential cutoff in all cases was 20Å, approximately $4.5\sigma_{\text{Max}}$, suggested for surface tension measurements using the coarse-grained water model. [102] The number of water coarse-grained beads in the system was 4800, corresponding to 9600 water molecules, and the number of surfactant molecules varied by system. The system box was created in accordance with studies that show a cell dimension of approximately $10\sigma$ is required to obtain accurate results for surface tension with implementation of periodic boundary conditions. [16, 180] Further information on how the system was generated can be found in Appendix A. Figure 5.3 is an illustration of a representative surfactant/water system.

At the conditions considered the density of air is low enough that, for the system size we studied, the amount of nitrogen/oxygen needed to reproduce that density would correspond to a fraction of a molecule. Adding a single nitrogen molecule would have essentially no impact on the results, and therefore we modeled air as vacuum. The bulk water box was 60Å wide, 60Å deep and 80Å long and was packed with 4,800 water beads. A simulation was run at 298.15K until the density was equilibrated (2 ns at a time-step of 1.0 fs). An interface was generated by extending the z direction to 3 times its original size creating regions of vacuum on either side of the water slab; the large vacuum regions was implemented to minimize packing issues when randomly packing surfactants in the vacuum region. A canonical simulation was then run for 4-8 ns at the same conditions.
Surface tension measurements of the water vapor-liquid interface were calculated to be within 5% of experimental results (model: 74.62 mJ/m², experimental: 71.97 mJ/m²).

Surfactants were packed randomly in the vacuum at a concentration specified separately for each system. An energy barrier was implemented 50 Å from the interface to prevent surfactants from migrating away from the interface; this is only likely to occur when randomly packing a large number of surfactants in the vacuum. Under these system conditions, the system energy was minimized for 3 ns to remove overlaps from randomly packed surfactants. All simulations were run at 298.15 K with a time-step of 2.0 fs. Surfactant molecules were gradually added to the system until critical surface adsorption was achieved. Further details on the method used to add surfactant molecules to the system can be found in Chapter 6. After the critical surface adsorption concentration was determined for the surfactant system, a final simulation was run for 2.5 ns to extract surface tension measurements.

5.3.2 Surface Tension Calculations

Surface tension values (\(\gamma\)) were calculated using the test area (TA) method. [52] This method uses a free energy perturbation to estimate the surface tension and has been validated for various types of interfaces. [162] The mathematical expressions used to calculate the surface tension are:

\[
\gamma \equiv \left( \frac{\partial F}{\partial A} \right)_{(N,V,T)} \approx \left( \frac{|\Delta F_+ - |\Delta F_-|}{2\Delta A} \right) + O(\Delta A)^2 \quad (5.3)
\]

\[
\Delta F = -kT \exp \left( \frac{-\Delta U}{kT} \right) \quad (5.4)
\]

Where \(\gamma\) is the surface tension and \(\Delta F\) is the change in Helmholtz free energy of the
Figure 5.2: Illustration of coarse grained beads compared to an all-atom representation. The surfactant consists of CM beads (teal), which behave like an alkyl chain, and OA beads (red: CH2OCH2, orange: CH2OH), which behave like an ethoxylated head group. Coarse-grained water beads represent two water molecules (blue). The atoms in the fully atomistic representation are color-coded as follows: oxygen (red), hydrogen (white) and carbon (teal).

system when the area of the interface that has been increased/decreased by the small increment $\Delta A$, while keeping the volume of the system constant. To determine $\Delta F$, the change in potential energy due to the perturbation, $\Delta U$, of the system is calculated during the simulation. [52] In this equation, $k$ is the Boltzmann constant and $T$ is the
Figure 5.3: Illustration of surfactant (teal, orange, red) and water (blue) system: entire box - including vacuum (left) and zoomed in on interface (right). The system dimensions are [60Å x 60Å x 600Å].

system temperature.

Numerical data needed to implement the TA method were calculated directly during the simulations by altering the area of the interface by changing the dimensions of the system (box length). Equation 5.3 and Equation 5.4 show the truncated perturbation expansion used to estimate the derivative of the free energy with respect to interfacial
Table 5.2: Surface tensions calculated for water and decanol-1 using the test area method, compared with experimental values (values in $mJ/m^2$)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Test Area</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>74.6 ± 0.2</td>
<td>71.97</td>
</tr>
<tr>
<td>n-Decanol</td>
<td>28.6 ± 1.3</td>
<td>28.51</td>
</tr>
</tbody>
</table>

area. The energy of the system was recorded for each area perturbation and the measurements were repeated 5000 times with 500 time-steps between each calculation (i.e. every 0.001 ns for 2.5 ns). For each perturbation, the system box was scaled by a factor of ±0.0005. To validate our simulations and verify the accuracy of the coarse-grained interaction potentials, we estimated the surface tension of water in equilibrium with vapor and decanol interfaces. Table 5.2 shows the surface tension measurements from the model and experimental analysis.

In this study, the surface tension was calculated via the test area method and mechanical route. All of the results obtained by two different methods (mechanical route and the test area method) were within 2% of each other and the test area results were used for the analysis.

5.3.3 Maximum Surface Adsorption ($\Gamma_{Max}$)

Effectiveness of a surfactant is quantified as the maximum reduction of surface tension. Experimentally, the surface tension reaches a minimum at the critical micelle concentration (CMC). Past the CMC, the concentration of surfactants at the interface remains constant and excess surfactant molecules group into micelles or aggregates. Figure 5.4 depicts the relationship between surfactant concentration and interfacial tension for ex-
perimental [176] and theoretical results.

As the concentration of surfactant increases on the surface, the interfacial tension decreases until a minimum is reached at which it becomes independent of concentration. This concentration is considered the CMC or maximum surface adsorption concentration ($\Gamma_{\text{Max}}$). Using molecular dynamics simulations, we are able to produce a similar plot. The x-axis in the plot for the simulated data is the number of surfactant molecules at the interface, whereas in the experimental plot, the x axis is representative of the total concentration ($\log c$) which is comprised of surfactants in the bulk aqueous phase and at the interface. In both cases, the surface tension is governed only by the maximum surface adsorption (max) of surfactant molecules and is not sensitive to bulk micelle concentration. [22, 78] Therefore, theoretically, we need only to simulate maximum surface adsorption to extract the minimum surface tension. Figure 5.5 shows the surface tension versus the number of surfactant molecules at the interface for four different surfactants.

![Figure 5.4: Comparison of measured surface tension versus surfactant concentration from data derived from experiment (left) [176] and data derived from molecular dynamics simulation (right).](image)
We observe that a plateau in the surface tension plot is not observed for every surfactant system, as depicted in Figure 5.5. Therefore, we derive a method for extracting the maximum surface adsorption concentration. Larger system sizes are required for micelle formation and computing $\Gamma_{Max}$ has a lower computational expense compared to the CMC.

5.3.4 New criterion for establishing the maximum surface adsorption ($\Gamma_{Max}$)

To determine the maximum adsorption concentration, we increased the number of surfactants on the interface until the surface became saturated and additional surfactants were unable to reach the interface. We established a quantifiable method to find this point in order to extract the concentration uniformly across all surfactants. To do this, we first calculated the radial distribution function (RDF) of the terminal head bead, used for all surfactants, to calculate the first hydration shell when submerged in box of water. The
RDF for the terminal head bead (OA) equilibrated in a slab of water \((g_{HW}(r))\) is shown in Figure 5.6.

![Figure 5.6: The radial distribution function for a terminal head bead (red) with surrounding water beads (blue). The first hydration shell is taken to have a radius of 5.5Å.](image)

Based on the RDF, the first hydration shell of the terminal head bead has a radius of 5.5Å. When a terminal head bead is at the water interface, the number of water beads within the first hydration shell radius will be high, on the same order as the number for an isolated head bead solvated in water. To visualize the density of water beads in the first hydration shell over the simulation, we use a histogram. A example histogram is shown in Figure 6.5. The y-axis on the histogram represents the percentage of surfactant molecules over 0.5 ns that contain 0-14 beads within the radius of the first hydration shell.

By examining the first hydration shell histogram for surfactants with differing topologies at increasing surfactant molecule concentration, we identified a criterion for determining surface saturation. Using the extracted percentages, depicted in Figure 5.5, we concluded that the surface tension levels off when the the percentage of surfactant molecules with zero or one beads in the first hydration shell reaches approximately 10-
Figure 5.7: A histogram showing the number of terminal head beads of the linear surfactant that have 0-14 water beads within the first hydration shell. The histogram was extracted from a simulation of 10 surfactant molecules equilibrated on the water vapor-liquid interface and averaged from data collected every 0.02 ns during a 0.5 ns simulation.

20%. In addition, we observe that for systems where surfactant molecules contain zero or one water bead in the first hydration shell for less than 10 percent of the 0.5 ns, the surfactant molecules are located predominantly at the interface. When the percentage exceeds 10% a significant portion of terminal head beads are not at the water interface and thus are not part of the surfactant monolayer. Therefore, we establish the criteria for the maximum surface adsorption ($\Gamma_{Max}$) to be the number of surfactant molecules (±2) at which the number of terminal head beads that have zero or one water beads within the first hydration shell (≤ 5.5 Å of OA) is 10%. In other words, maximum surface adsorption is achieved when the number of surfactant molecules not located at the water interface equals 10%. To illustrate, this percentage and surface tension are plotted versus
the number of surfactant molecules in Figure 5.8. As the number of surfactant molecules in the system increases, the number of surfactant molecules having zero or one water bead in the first hydration shell increases since space on the water surface is less readily available due to packing effects. Illustrations of the surface as the number of surfactant molecules increases for C₃EO₄ are shown in Figure 5.9.

Figure 5.8: The percentage of surfactant molecules with zero or one water bead in the first hydration shell for 10 to 135 surfactant molecules (black) and surface tension (grey) versus number of surfactant molecules at the interface for linear AE’s: C₃EO₄, C₄EO₄, and branched AE: C₃EO₃.

Figure 5.9: Illustrations of interface for surfactant C₃EO₄ with 80 surfactant molecules (7%), 95 surfactant molecules (12%) and 135 surfactant molecules (26%) at the water interface.
5.4 Results

5.4.1 Linear $\Gamma_{Max}$ and $\gamma$:

We tested the method for determining $\Gamma_{Max}$ on systems with linear surfactants and increasing tail length. Figure 5.10 shows $\Gamma_{Max}$ vs. tail length (left) and surface tension ($\gamma$) versus $\Gamma_{Max}$ (right) for increasing tail length. For increasing tail lengths, effectiveness is shown to decrease (i.e. $\Gamma_{Max}$ surface tension values increase), which is in agreement with experimental observations. [146]

Figure 5.10: Maximum surface adsorption ($\Gamma_{Max}$) versus the number of coarse-grained tail beads and surface tension versus ($\Gamma_{Max}$) for linear surfactants.
5.4.2 Head Group Analysis

Industrially, surfactant head bead length (OA, EO) ranges from three to twelve beads. [60, 18] Surfactants with two, three and four head beads were analyzed for a range of tail bead number for linear and Guerbet (T-shaped) type. The plots in Figure 5.11 show that linear, or unbranched, surfactants with a constant number of head beads and increasing number of tail beads (i.e. C$_{2-7}$EO$_{3,4,5}$) behave according to the following trends: increasing tail bead number past a 1:1 head-to-tail ratio decreases effectiveness (e.g. $\gamma_{\text{min}}$(C$_3$EO$_3$) = 31 mJ/m$^2$ and $\gamma_{\text{min}}$(C$_6$EO$_3$) = 43 mJ/m$^2$); increasing tail bead number decreases the number of surfactant molecules needed for maximum surface adsorption (e.g. $\Gamma_{\text{Max}}$(C$_3$EO$_3$) = 93 and $\Gamma_{\text{Max}}$(C$_6$EO$_3$) = 85); and for the same number of tail beads, per molecule the more effective surfactants have 4, then 3, and lastly 2 head beads (e.g. $\gamma_{\text{min}}$(C$_5$EO$_4$) = 16 mJ/m$^2$, $\gamma_{\text{min}}$(C$_5$EO$_3$) = 40 mJ/m$^2$ and $\gamma_{\text{min}}$(C$_5$EO$_2$) = 60 mJ/m$^2$). If the number of head beads exceeds four, surfactants with less than eight tail beads (C$_{x<8}$EO$_{n>4}$) are water soluble. The ratio of head beads to tail beads is equal for C$_2$EO$_2$, C$_3$EO$_3$, C$_4$EO$_4$; however, C$_4$EO$_4$ exhibits a stronger interaction with water and hence is more effective. Altogether, surfactants with four head beads are shown to be the most effective, but those with three and two head beads exhibit similar trends.

For linear surfactants with high head to tail ratios, when the tail–tail interaction becomes stronger than that of the head-water, the head-water interaction is decreased and they become less effective. [162] This is in accordance with a conclusion drawn by Lin et al that surfactants with greater than 16 alkyl groups have an increased tendency to tangle around themselves; thus reducing the effective interaction with the polar substance. [99, 162]

The length of Guerbet-type (T-shaped) surfactants was tested for surfactant molecules
with three and four head beads. For the head group analysis, branched surfactants are identified as \#B\#M:\#H, i.e. \[# branch beads\] \[# numerical location on the backbone\]: \[# head beads\]. The plots shown in Figure 5.12 show an increasing surface tension for increasing branch length. We see a similar exception to that of linear surfactants where those with a greater number of head beads than branch beads have a less obvious surface tension trend, i.e. 1B1M:3 (two total branch beads and three head beads) versus 2B1M:3.
(four total branch beads and three head beads. However, in this case, all surfactants have a smaller or equal number of head beads to total number of tail beads, i.e 1B1M:3 has a 3:3 ratio of tail to head beads, except 1B1M:4, which is soluble in water.

Figure 5.12: Surface tension ($\gamma$) versus maximum surface adsorption ($\Gamma_{Max}$) for surfactants with three (left) and four (right) head beads and increasing branching length on one backbone bead (3:1, 4:1).
For surfactants with a symmetric branch on a single backbone bead (Guerbet-type, T-shaped), decreasing the length of the branch increases effectiveness, except in cases where the number of beads in the branch is less than the number of beads in the head group. In addition, for surfactants with equal number of branch beads, increasing the number of beads in the head group increases effectiveness.

5.4.3 Tail Group Analysis

To analyze the effect of tail group topology, we chose to use surfactants with three head beads. Although three head group beads fall on the lower end of the number of head group beads in industrial surfactants and are less effective than those with four head beads, as depicted in Figure 5.12, using surfactants with three head group beads allows us to explore surface tension trends while also minimizing the computational expense. As for the number of tail beads on the modeled surfactants, the majority of AE production for household cleaning products (>60 percent) consists of 12-14 carbon atoms in the tail group. This would fall between three and four coarse-grained beads; therefore, the linear portion of tested surfactants is between one and four beads. For the tail group analysis, branched surfactants are identified as \#B\#M:\#T, i.e \(#\) branch beads \[#\] numerical location on the backbone\: \[#\] tail beads\.

An advantage to branching is the ability to sample a range of surface tension values using identical chemical composition. Figure 5.13 depicts the range of values accessible to surfactants with a composition of C\textsubscript{8}EO\textsubscript{3}. To provide insight into the topological effect of branching on surface tension, we present a series of plots and density profiles for subsets of the 100+ surfactants analyzed. A table with data for all surfactants studied can be found in Appendix A.
Adding branches allows for a larger range of $\Gamma_{\text{Max}}$ and $\gamma_{\text{min}}$ using a constant number of head and tail beads. Being able to clearly identify topologies that will result in low surface tension at reasonable $\Gamma_{\text{Max}}$, and therefore CMC values, prior to experimental analysis is highly advantageous because surfactants with desirable properties can be chosen computationally, reducing experimental expense. Using the trends observed in the surface tension vs. $\Gamma_{\text{Max}}$ plots, we have identified that adding a single one bead branch to the tail bead adjacent to the head group, 1B1M:4, results in a $\gamma_{\text{min}}$ of 42.4 mJ/m$^2$ and at the outermost tail bead, 1B4M:4 results in a $\gamma_{\text{min}}$ of 32.7 mJ/m$^2$) does not increase effectiveness in comparison to the analogous unbranched surfactant, 0B0M:4 which has a $\gamma_{\text{min}}$ of 33.0 mJ/m$^2$.

Figures 5.14 depicts the surface tension for single-branched surfactants with increasing number of branch beads at the same distance from the tail-adjacent head bead (i.e. 1B1M:4, 2B1M:4). 5.15 depicts surface tension trends for single-branched surfactants with the same number of branch beads at increasing distance from the tail-adjacent head bead (i.e. 1B1M:4, 1B2M:4). From these plots, we see that surfactants increase in efficiency as the branch is moved further away from the tail-adjacent head bead (i.e. 1B2M:4 is more efficient than 1B1M:4). However, in all four cases, a branch location farthest from the tail-adjacent head bead (i.e. B4M:4) results in an outlier where the surface tension is 12-15 mJ/m$^2$ higher than expected according to the curve. In addition, surfactants with one branch bead (1BM:4) are able to achieve the lowest surface tensions and thus are the most effective. However, these also require a larger number of surfactants molecules to achieve maximum surface adsorption. Furthermore, we see that a surface tension of 25 mJ/m$^2$ can be achieved using three different topologies: 1B2M:4, 2B3M:4, and 3B3M:4 at $\Gamma_{\text{Max}}$ values of 79, 81, and 75, respectively.

The plots in Figure 5.15 exhibit a decreasing curve where decreasing branch
bead number at the same location (i.e. 3B1M:4 versus 2B1M:4) increases efficiency. Surfactants with branch located on the third backbone bead (XB3M:4) are able to achieve the lowest surface tension and those that have a branch bead neighboring the head group (XB1M:4) or on the last tail bead (XB4M:4) are the least effective.

Figures 5.16 and 5.17 illustrate the effect of adding linear beads above or below a
Figure 5.14: Surface tension ($\gamma$) versus maximum surface adsorption ($\Gamma_{Max}$) for single-branched surfactants with an increasing number of branch beads located on the first linear bead (upper left), second linear bead (upper right), third linear bead (bottom left), and fourth linear bead (bottom right) from the tail-adjacent head bead. The linear AE with three head beads and four tail beads has a $\Gamma_{Max}$ of 92 and $\gamma$ of 32.97 mJ/m$^2$. 
Figure 5.15: Surface tension ($\gamma$) versus maximum surface adsorption ($\Gamma_{\text{Max}}$) for single branched surfactants with one branch bead ($C_6\text{EO}_3$, upper left), two branch beads ($C_8\text{EO}_3$, upper right), three branch beads ($C_{10}\text{EO}_3$ bottom left), and four branch beads ($C_{12}\text{EO}_3$, bottom right) located one, two, three, and four beads away from the tail-adjacent head bead. The linear AE with three head beads and four tail beads has a $\Gamma_{\text{Max}}$ of 92 and $\gamma$ of 32.97 mJ/m$^2$. 
one bead branch. Figure 5.16 shows that increasing the length of the backbone past the single branch (i.e. 1B1M:1, 1B1M:2, 1B1M:3) decreases effectiveness, whereas increasing the number of beads below the branch (i.e. 1B1M:1, 1B2M:2, 1B3M:3) has less variation in $\Gamma_{Max}$ and surface tension; however, in comparison to a branch with one bead versus two, there appears to be an optimal relationship between number of beads in a branch and the number of backbone beads below the branch. For example, in Figure 5.17 for surfactants with one bead in the branch, 1B2M:2 is most effective; and for surfactants with two beads in the branch, 2B3M:3 is most effective.

Figure 5.18 shows that increasing the density of one bead branches on a single surfactant (i.e. 1B1M_1B2M:4, 1B1M_1B2M_1B3M:4) has little correlation with effectiveness.

Figure 5.16: Surface tension ($\gamma$) versus maximum surface adsorption ($\Gamma_{Max}$) for single-branched surfactants with increasing number of backbone beads past the single branch for branches with one bead (top left) and two beads (top right).

---

Surface Tension (mJ/m²)

<table>
<thead>
<tr>
<th>One Unit Branch</th>
<th>Two Unit Branch</th>
</tr>
</thead>
<tbody>
<tr>
<td>53, 44.1</td>
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<tr>
<td>57, 41.8</td>
<td>37, 41.8</td>
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<tr>
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<td>68, 36.3</td>
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<td>80, 27.0</td>
<td>82, 25.3</td>
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<td>91, 23.1</td>
<td>91, 23.1</td>
</tr>
</tbody>
</table>
Figure 5.17: Surface tension ($\gamma$) versus maximum surface adsorption ($\Gamma_{\text{Max}}$) for single-branched surfactants with increasing number of backbone beads prior to the single branch for branches with one bead (top left) and two beads (top right).

However, it should be noted that, in all these cases, there is a branch located on the first linear bead, which was shown previously to be least effective in reducing the surface tension, and the least effective surfactant has a branch located on the top most and bottom most tail bead.

Figure 5.19 illustrates the relationship between the spacing distance of branches with two beads. We see that the surfactant with branching on the top and bottom (2B1m–2B4M:4) is the most effective out of this set.
Figure 5.18: Surface tension ($\gamma$) versus maximum surface adsorption ($\Gamma_{\text{max}}$) for surfactants with four backbone beads and increasing number of one bead branches.

5.4.4 Discussion:

In this paper, we have reported molecular dynamics results that provide insight into the relationship between branching of ethoxylated surfactant molecules and reduction of surface tension at a water vapor-liquid interface for water. To aid in this section, we provide an overview of surface tension to help explain the topological trends we observed between branched surfactants and surface tension measurements.

The chemical duality of surfactants, which are composed of a hydrophilic, water-
Figure 5.19: Surface tension ($\gamma$) versus maximum surface adsorption ($\Gamma_{\text{Max}}$) for surfactants with four backbone beads and differing distance between two branches consisting of two branch beads.

Compatible portion and hydrophobic, oil-compatible portion fosters an association between two ordinarily incompatible materials, such as oil and water. When submerged in a system containing an oil-like and water-like substance, surfactants seek to reduce free-energy, or strain, by orienting the portion of their chemical make-up in the substance that allows for optimization of the number of surfactant molecules ($\Gamma_{\text{Max}}$). At the interface, a greater attraction exists between similar molecules (cohesion) than between
dissimilar molecules (adhesion) creating an imbalanced force at the interface between dissimilar molecules. The tension at the surface caused by the imbalanced cohesive forces can be measured as the surface tension. This tension can be reduced by weakening the inward forces by incorporating molecules with dual compatibility (surfactants) which promote adhesion between dissimilar molecules. The optimal surfactant, which maximizes reduction of the surface tension, strongly and equally interacts with both materials. If a stronger attraction exists between the hydrophilic or hydrophobic portion, an inward force will continue to exist. Using this analysis of surface tension and surfactants, we are able to explore the trends shown in the results section.

Linear, or unbranched, AE surfactants have the least structural variance with the only variable being the length of the tail and length of the head portion. As the length of
the tail bead increases, the flexibility of the tail increases the tail-tail interaction between surfactant molecules increases, which increases the strength of hydrophobic interaction versus the hydrophilic. If the number of head group beads in a surfactant molecule is held constant while varying the tail length, there exists an optimal ratio of head to tail beads for surface tension reduction. Past that ratio, the strength of the hydrophobic interaction exceeds that of the hydrophilic interaction resulting in a reduced interaction between the head group and water and vice versa.

Incorporating branching into AE surfactants significantly broadens the number of possible surfactant structures. Adding a single branch to linear AE’s gives unique insight into the behavior of surfactants. By holding the backbone length and head length constant and varying the length/location of a single branch, the following observations were made:

1) If a single branch is on the first backbone bead from the tail-adjacent head bead and has additional backbone beads (cross-like shape), the branch is sterically strained to interact close to the interface. Repulsion between the branch and the polar substance results in a weakened interaction between the head portion and polar substance. Consequently, these surfactants are less effective.

2) If T-shaped, the branch is not sterically restricted and so has the freedom to explore more favorable configurations resulting in a more linearly stretched arrangement (Y-shape). Therefore, increasing branch length on the outermost tail bead has a similar effect to increasing length of a linear AE’s, which becomes ineffective past the optimal head to tail bead ratio.

3) If located in the mid-region of the backbone, the mobility of the branch is sterically restricted promoting a stronger tail-tail interaction near the interface while allowing the head beads to remain submerged in the polar component as it would be for the linear AE equivalent. However, if the branch exceeds optimal length, which is dependent on
position with respect to the head bead, the number of surfactant molecules that can pack at the interface becomes limited and lessens head bead interaction; hence, longer branches require longer head beads for a stronger polar interaction. Therefore, for mid-region branching, length of branch, location with respect to head bead and packing density are variables of effectiveness.

From the single branch analysis, we can conclude that a stronger nonpolar interaction closer to the interface, which in some cases is encouraged by branching, increases effectiveness; however, a counter-effect occurs if the nonpolar interaction impacts the strength of the head group interaction.

Guerbet type surfactants behave similar to the T-shaped surfactants mentioned previously. They have a one backbone bead with a single branch that is adjacent to the head group. This type behaves similar to linear AE’s since the branch is not sterically hindered, allowing the branch to relax away from the interface. However, this type is more sterically limited than the linear AE with equal number of nonpolar beads (i.e. $\gamma(C_5EO_3) > \gamma(C_5EO_3)$) and is more effective.

Qingzhao et al. studied the solubility of nonionic hydrocarbon surfactants and concluded that surfactants with asymmetric branched chains provide the worst solubility due to largest attractive molecule-molecule interactions and that an increase in alkyl chain length has a negative effect on solubility; the attractive interaction between tail groups followed the order Guerbet type (T-shape) $C_{16}EO_6$ is greater than linear tail $C_{14}EO_6$. [162] They found that the surface tension was 3 mJ/m$^2$ less for the Guerbet type than linear type. Similarly, we see that for the same number of head and tail beads, effectiveness follows the same order: Guerbet type is greater than linear type. In their study, they also postulated that branched surfactants were more effective because they form a hydrophobic surfactant layer that was more densely packed in comparison to linear. [162]
In addition to single branches and Guerbet type (T-type), increasing the density of branches past one branch restricts the flexibility of the surfactants making it less favorable for surfactant molecules to pack together on the surface. Increasing branch density therefore increases rigidity which in turn decreases flexibility making the surface less accessible to surfactant molecules. Therefore, $\Gamma_{Max}$ is lessened and the potential head group interaction is decreased.

In the case of two branched AE’s, a branch located at the top and bottom tail bead has the most flexibility and the top branch has an effect of restricting mobility of the lower branch, increasing tail interaction near the interface. The spacing between branches is therefore an important factor in head-tail interaction; branches too close together increase tail-tail interaction, but decreases mobility and branches far from each other ineffectively increases the head to tail ratio.

The low surface tensions ($\gamma(1B3M:4)=20.3 \text{ mJ/m}^2$, $\gamma(2B3M:3)=18.1 \text{ mJ/m}^2$ and $\gamma(1B1M:1)=23.1 \text{ mJ/m}^2$) and corresponding density profiles, illustrated in Figure 5.20, indicate that widening of interfacial region and overlap between the tail-head region is an effect of surfactants with higher efficiency (i.e. lower surface tensions at the water vapor-liquid interface). In other words, surfactants that effectively reduce surface tension have an effect of widening the interfacial region.

### 5.5 Conclusions

We have presented results from coarse-grained molecular dynamics simulations illustrating the relationship between the tail group topology of ethoxylated surfactants and the ability to lower surface tension at the water vapor-liquid interface. We find that branching of AE surfactants allows for a range of water vapor-liquid surface tension values ranging
from 10 mJ/m² to 65 mJ/m². Our results indicate that branch location and head to tail bead ratio significantly impact a surfactant’s ability to lower the surface tension at the vapor-liquid interface of water. Furthermore, the more effective surfactant topologies enable a strong tail-tail interaction without interfering with the head-water interaction. For example, a branch that is constricted adjacent to the head group (cross-shaped) has a negative effect of reducing the interaction between the head group and water because of the repulsive interaction between the branch and water. Furthermore, surfactants that effectively reduce surface tension have an effect of widening the interfacial region. Conclusions drawn from this study can be applied to surfactant design in the effort to replace perfluorinated surfactants. The method used to obtain these results is also a first step toward the development of a predictive model connecting the topology of surfactants with interfacial tension.

5.6 Future Directions

In this paper, we have developed a thorough understanding of surfactant branching features that lead to optimal behavior. We have presented results from 100+ coarse-grained simulations exploring the connection branched alcohol ethoxylates and provided insight into the behavior of branched and linear surfactants at the water vapor-liquid interface. The key findings can be used to develop a general equation for linking AE topology with effectiveness, which can be implemented into an automated search tool to rapidly investigate a broad scope of topologies and predict new surfactants. A genetic algorithm is a great tool that can be used to automate the search of chemical space for optimal surfactants. [130, 154] Key principles for the accuracy of a predictive model are first the size and quality of the database and second the calculation of relevant descriptors.
Compounds in the database must be representative of chemical families targeted in the study. [7]

In addition, the method applied to study branching of AE’s can be employed to re-
search various surface-active agents including polymers, perfluorinated compounds, ionic
compounds, peptides, etc. as long as interaction parameters exist. The chemical make-up
of the bulk components and compounds can be varied to study a large scope of systems.
Furthermore, SAFT-\(\gamma\) interaction parameters exist for a database of coarse-grained chem-
ic beads. The following systems are recommended as areas of potential interest:

1) The optimal surfactant is one that weakens the imbalanced cohesive forces, there-
fore it is proposed that a surfactant with a hydrophobic, hydrophilic and hydropho-
bic/hydrophilic region, such as the one shown below, has the potential to decrease the
surface tension below that of contemporary surfactants.

![Proposed structure for surfactant with hydrophobic, hydrophilic and a hy-
drophobic/hydrophilic region](image)

Figure 5.21: Proposed structure for surfactant with hydrophobic, hydrophilic and a hy-
drophobic/hydrophilic region

2) The procedure for studying surfactant tail group topology can be employed for
the chemical composition of the head group. The coarse-grained interaction parameters
of the head bead can be varied to optimize the chemistry for different chemical environ-
ments. This can also be applied to the tail group, although it has been determined that
fluorinated tail groups are resistant to biodegradation [REFERENCE].

3) Perfluorooctanoic and perfluorooctanesulfonic acid (PFOA, PFOS) have fully fluorinated alkyl chains and are used in the fabrication of Teflon and other products, such as fabric protectors. These compounds have been shown to be bioreistant and show evidence of carcinogenicity [REFERENCE]. Compounds with partial fluorination may be just as efficient while also offering higher degradation potential. This is an area that can be investigated using the above computational approach. An investigation into the behavior of fully fluorinated compounds would be beneficial in determining whether these compounds can be replaced with partially fluorinated or branched alkyl-based surfactants.

5.7 Acknowledgements

This work has been partially supported by a Doctoral New Investigator grant from the American Chemical Societys Petroleum Research Fund (#55801-DNI6). The molecular graphics in this work were created using Visual Molecular Dynamics (VMD). [70]
Chapter 6

AutoSurf: Automated Generation and Analysis of Large-Scale Coarse-Grained Molecular Dynamics Models of Surfactant Systems;
Version 1.0

Mariah J. King, Cody K. Addington, Nathan C. Duff, Erik E. Santiso

6.1 Abstract

In this work, we present AutoSurf, a python package designed to facilitate system generation, simulation and analysis of systems containing polymers or surfactants at an interface. AutoSurf is designed to smoothly integrate user input, python scripts, highly
optimized third party open-source software and post-simulation analysis. The tool enables a standardized methodology by which saturation of the surface and interfacial tension measurements can be obtained through molecular dynamics simulations. The package has been successfully implemented to study over 500 systems containing surfactants with varying topology at a water vapor-liquid interface.

6.2 Introduction

As the variety of interesting systems at the interface being studied increases, more general and automatized approaches will be of great utility in research efforts. Understanding the underlying aspects of interfacial systems requires information on both the spatial organization and temporal dynamics. Molecular dynamics (MD) play an important role in studying these many-body problems by examining the motion of individual particles using a molecular-scale model to study system behavior across spatiotemporal domain length scales and time scales. Automated computational tools that integrate interfacial systems and molecular dynamics simulations offer the ability to generate standardized information for a variety of systems using specified design criteria.

In this chapter we introduce a computational platform that allows for high-throughput exploration of thermodynamic properties of homo- and hetero- polymer systems or surfactants at an interface using a well established molecular dynamics simulator to gain a microscopic understanding of the properties of these everyday materials. Development of molecular dynamics models is a lengthy process involving multiple steps and user input. In addition, input parameters for molecular dynamics simulators have to be specified for each system. Overall, the process is tedious, time-consuming and subject to user error which leads to wasted time and computational resources. Implementation of the auto-
 automated platform to generate system configurations and input scripts reduces the possible systematic error and enables rapid submission of numerous surfactant systems in a short time frame. [136, 106] The motivation for the development of this tool was to design a automated computational platform to assist in the discovery of surfactants for the replacement of perfluorinated tail groups in CO$_2$ emulsion. Therefore, the tool was originally developed to study ethoxylated surfactants at the water vapor-liquid interface, thus it reflects the analysis techniques used to conduct that specific research project but can be easily modified for additional chemical systems, including polymers, and additional interfaces, including CO$_2$-water interfaces.

We present our tool as series of scripts that can be used in its present condition or adapted to the users specific system. The tool is used in combination with previously designed open source codes including LAMMPS, a customizable molecular dynamics simulator; PACKMOL, a code designed to minimize packing issues in densely arranged molecules; and Moltemplate, a molecule builder. [112] Incorporation of these established tools significantly influenced code development and the successful exploration of surfactant topologies presented in the previous chapter. Using python as the primary source code stemmed from the desire to create a user-friendly platform to encourage rapid exploration of diverse interfacial systems without having to worry about the more involved syntax. A File formatting, organization and execution is incorporated into the package so users only have to define the topology of the surface active agent and the interfacial parameters. For advanced users, the option also exists to adjust additional input parameters for the simulation environment and force field parameters. However, version 1.0 of AutoSurf is primarily designed to model polymers or surfactants with a simple chemistry at an liquid-vapor interface. The tool has the potential to be extended to systems with more complex chemistries using a database of coarse-grained potentials.
Here, we describe the Automated Surfactant (AutoSurf) building tool and repository. AutoSurf is a package that can provide topologies for a small set of polar and non-polar parameters that can be used to describe a wide range of polymer or surfactant systems. The system generator is integrated with the molecular dynamics simulator, LAMMPS, to allow for the efficient simulation and generation of density profiles and surface tension data. Autosurf has three primary functions: first, to generate starting configurations for any molecular simulator; second, to generate input scripts for LAMMPS that include compute commands to generate data collection during the simulation; third, to analyze data post-simulation. This tool was designed to efficiently gather interfacial saturation and surface tension data for a wide range of surfactant topologies. However, the tool has been generalized so it may also be applied to study systems of polymers at an interface.

6.3 Molecular Model and Methodology

Suppose we want to understand the behavior of a linear hetero-polymer system at the water vapor-liquid interface using molecular modeling. This would require building a geometric configuration that accurately represents the dynamic system. To do this, we need to define parameters that describe the intramolecular and intermolecular interactions, including bond length, bond angles, van der Waals forces, etc. Numerous models to describe these interactions have been developed, two approaches being fully atomistic or coarse-grained based. In coarse-grained models, groups of atoms are parameterized into 'beads' to reduce the degrees of freedom. Coarse-grained molecular dynamics were chosen for our study since this approach allows for increased computational efficiency and bridges the gap between micro and macro scale system properties. Additionally, this approach allows for a similar investigation of large-scale systems to that of conventional
atomistic models while remaining computationally affordable. Two approaches exist for deriving coarse-grained parameters: “top-down” and “bottom-up”. For this specific system, we chose to use force field parameters estimated using a “top-down” approach called group-contribution SAFT-\(\gamma\) Mie equation of state (EoS). [104, 102] This model has been shown to successfully reproduce macroscopic thermodynamic experimental data for complex real fluids and to predict properties that are not accessible from the equation of state, such as interfacial and dynamic properties. This method is discussed further in section 6.3.1 and has been used to derive a library of parameters for nonpolar and polar components often used in the chemical synthesis of polymers and surfactants.

6.3.1 SAFT-\(\gamma\) Mie model and theory

Our tool uses a well-established coarse-grained model, Statistical Associating Fluid Theory (SAFT), to describe the thermodynamics and fluid-phase equilibria of systems with polymers or surfactants at an interface. Inspired by the Wertheim’s first order thermodynamics perturbation theory derived to describe classical fluids of molecules that tend to associate into dimer and higher order groups due to highly directional attraction, Gubbinss et al. proposed the Statistical Association Fluid Theory (SAFT) [122, 110, 111] to describe the thermodynamic and fluid-phase equilibria of spherical and chain molecules with one or more highly directional attraction, such as hydrogen-bonding. In this theory, associating contributions are based on the perturbation theory in which the chain contribution can be obtained from the association bonds. For the monomer term, the hard sphere fluid is chosen as a reference and the real fluid behaviour can be expressed by the residual Helmholtz Free energy.
\[
\frac{A}{NkBT} = \frac{A_{\text{Ideal}}}{NkBT} + \frac{A_{\text{Mono}}}{NkBT} + \frac{A_{\text{Chain}}}{NkBT} + \frac{A_{\text{Assoc}}}{NkBT}
\]  

(6.1)

where \(A_{\text{ideal}}\) is the free energy of the ideal gas, \(A_{\text{mono}}\) is the term accounting for interactions between monomeric Mie segments, \(A_{\text{chain}}\) is the contribution to the free energy for the formation of molecules from Mie segments, \(A_{\text{assoc}}\) is the term accounting for the association interactions, \(N\) is the total number of molecules, \(k_B\) is the Boltzmann constant, and \(T\) is the absolute temperature. The parameters that describe the contribution of each functional group to the molecular properties are typically estimated from appropriate experimental data. A comprehensive review on the expansion of the free energy term can be found in reviews by Economou and Papaioannou. [131]

The third generation of the theory, SAFT-\(\gamma\) incorporates a group-contribution method, thus, allowing for treatment of heteronuclear molecules formed from segments of differing chemical functionality. [104, 102, 95, 4, 5, 122, 61, 131, 123] The integration of group contribution and SAFT allowed for accurate models for thermodynamic properties and phase equilibrium properties of homo- and hetero- compounds and mixtures over a range of temperatures and pressures. A detailed description of the group contribution can be found in the review by Papaioannou et al. [131]

In our case, we use three coarse-grained beads to describe the heteronuclear compounds: one to describe nonpolar beads and two to describe polar beads. The interface, in this case a water vapor-liquid interface, is described using a single bead composed of two water molecules, also known as the water dimer. The interaction parameters for the four beads are listed in Table 5.1 and the beads interact according to the Mie \(\lambda_a - \lambda_b\) potentials as shown in Eq. 5.1. [115]
6.4 System Building

A flow-chart outlining the steps for system generation, simulation and analysis using AutoSurf is provided in Figure 6.1. The input information required by the user is in Table 6.1. The procedure is described in the following ten steps.

In **Step 1**, a general structure for the polymer or surfactant (not including xyz coordinates) is read in and, through a series of run scripts, an xyz file and input files for PACKMOL are generated. In **Step 2**, the molecule XYZ file and a pre-built, equilibrated XYZ file of bulk fluid is used as an input files for PACKMOL, a tool used to efficiently pack arbitrary molecules in a three-dimensional region, and outputs an XYZ file. In **Step 3**, Moltemplate is used to generate LAMMPS input files from the xyz coordinates, bond, and angle information provided by the user. In **Step 4**, an executable file submits the initial system minimization to LAMMPS. In **Step 5**, compute commands in the input file for LAMMPS generate density data and pair correlation information for specified units. In **Step 6**, the submission file for LAMMPS calls a script that analyzes the output data from the LAMMPS simulation and uses a criteria to determine the success of the simulation. In **Step 7**, if the set criteria is not achieved, a script is run that increases the number of molecules in the system by a user-specified number. In **Step 8**, the newly generated system is simulated in LAMMPS to generate additional density data and pair correlation information. In **Step 9**, the simulation criteria is met and the executable file calls a separate LAMMPS input script that generates data for surface tension measurements. In **Step 10**, the submission file outputs the final surface tension value at the maximum surface adsorption concentration. Figure 6.1 illustrates the process described in the steps above. In the following section, the above steps will be described in detail.
6.4.1 Input Parameters

The input parameters that can be easily adjusted based on the system the user desires to study are shown in Table 6.1. Detailed descriptions on each variable input are included.

Figure 6.1: Diagram illustrating the steps taken to generate, simulate and analyze surfactant-mediated interface system.
in Section 6.5.

Table 6.1: Input parameters used by the source files to generate geometry and input files for PACKMOL, Moltemplate and LAMMPS.

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<tr>
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<th>Variable Input</th>
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</table>
The structure files and input parameters will be discussed in more detail in section 6.5.
Figure 6.2: (a) input format for generating single molecule xyz file and (b) output chemical structure generated from input file. For the input format, 'NP' corresponds to linear nonpolar beads, 'B' corresponds to nonpolar branch beads, 'P' corresponds to polar beads and 'T' corresponds to the terminal polar bead.

6.5 Code Development

During the initial step, the user inputs a text file containing minimal information on the structure of the molecule. An example of the input file is shown in Figure 6.2

In this file, 'NP' represents 'Nonpolar' groups, 'P' represents 'Polar' groups and 'T' represents the 'Terminal' polar group. Using the correct syntax for the above groups is crucial for the python script to run without error. In addition, the terminal polar bead is used to generate information processed during the criteria step, therefore it is essential to define the terminal polar bead using the 'T' syntax and should only be used once.

From this file, coarse-grained bead coordinates, bond data and angle data is generated and formatted into an xyz file and a PACKMOL input file. The input data required for
PACKMOL is shown in Table 6.1.

The packmol tolerance defines the distance that all atoms will be to each other in the final structure to be 4.5Å. The bead distance provides that the bond distance between beads within a molecule is 4.5Å. The monomer space provides that the molecules should be placed inside a cube with minimum coordinates \((x,y,z) = (25,25,45)\) and maximum coordinates \((25,25,135)\). The surface boxsize provides that the surface, in the surface filename 'w_60xy80z.xyz', has minimum coordinates \((x,y,z) = (-30,-30,-40)\) and maximum coordinates \((30,30,40)\) and contains 4,800 beads. The overall system size has minimum coordinates \((x,y,z) = (-30,-30,-300)\) and maximum coordinates \((30,30,300)\) including vacuum. The system box was created in accordance with studies that show a cell dimension of approximately 10\(\sigma\) is required to obtain accurate results with implementation of periodic boundary conditions. [16, 180]

The python scripts used to generate structural information can be found at https://github.com/mjritz/AutoSurf. The key element in the initial script is cycling through each line of the text file in Figure 6.2 to identify each xyz coordinate according to its position relative to the first backbone component 'NP' encountered. In the above example, the 'T' on line 1 is the first backbone component. From the xyz coordinates, the beads are appointed a number based on their identification syntax (NP, P, T). For this reason, topologies are restricted to identical repeating monomer units, i.e. there cannot be nonpolar groups that are separated by polar groups (NP-P-NP). Additionally, branching of polar groups has not been incorporated into the first version of the software, therefore 'B' can only be placed next to 'NP' groups.

The default interface is the water vapor-liquid interface where the water slab has dimensions of 60Å in the x and y direction and 80Å in the z direction. The xyz coordinates for the equilibrated water slab can be found at https://github.com/mjritz/AutoSurf. This
method can in principle be applied to other coarse-grained fluid systems.

In cases where the user specifies a new interface, PACKMOL requires that the user specify the minimum and maximum three dimensional values that molecules may be packed within and a requisite is that the interface be oriented in the z direction. Furthermore, the distance tolerance for the molecules being packed into the three dimensional space can be adjusted. The default distance tolerance is based on the largest \( \sigma \) value (NP-NP); this may be adjusted to smaller values to pack more molecules into a given space, but may take a longer time to meet the packing criteria and reach an equilibrated state in a molecular simulation.

During the third step, Moltemplate, a general cross-platform text-based molecule builder for LAMMPS, is called upon by the executable file to generate input geometry file for LAMMPS. The xyz file created by PACKMOL is used to generate input files for Moltemplate, which outputs a LAMMPS formatted input files. Automation of this process is highly beneficial since it can be time intensive especially for highly bonded molecules since it requires intermolecular interaction parameters, i.e. bond distances and bond angles.

The bond coefficients, angle coefficients and atomic masses for the system studied are shown in 6.1. Each input script for Moltemplate is named according to the information the file contains. For example, 'mie_ff.lt' contains mie force field parameters for the system and 'monomer_struct.lt' contains structural information for the monomer. The force field input file contains atom mass; bond coefficient; and angle coefficient data that is written to the LAMMPS data file. If the user does not desire to change the chemistry of the components, this file does not need to be adjusted. The average values of the spring constants and the bending angles were obtained by Lobanova et al. from a fit to a Gaussian distribution function and were determined to be 7.583 and 2.650 \( \frac{kcal}{mol\cdotÅ^2} \).
respectively. An optimized bond angle has only been defined using the SAFT\textsubscript{γ} force field for the alkyl, or nonpolar bead, so it is fixed within the program. The bond distance is set at a defaulted length of (4.36Å) since it corresponds to the maximum σ value, the finite distance at which the interparticle distance is equal to zero, which in this case is for two nonpolar beads. This value is appropriate for all other coarse-grained interactions and allows for the system to equilibrate to a minimized state without imploding. However, the closer this distance is to the equilibrated bond distance, the more quickly the system will reach its equilibrated state.

During the fourth step, an executable file creates a subdirectory in which to organize all the system specific files, simulation files and post-processing files. This script then submits the LAMMPS job. The first version of AutoSurf has been written on a high performance cluster with a platform data manager for a load sharing facility (LSF). Therefore, the command used to submit the LAMMPS job is specific to the IBM platform manager for LSF.

### 6.5.1 Default LAMMPS Settings

System specific variables for LAMMPS are included in 6.1. They are described here in order of appearance. The units per molecule and the units in the backbone have to be set per molecule and are used in the python scripts that add additional molecules to the surface. The temperature of the system is set to a default of 298.15K. and the equilibration times can be adjusted under the variable names long\_equilibrate and short\_equilibrate. The long equilibration is done after the first initial packing when the molecules are spread out across the vacuum. During this equilibration step, an energy wall is used as a boundary for the packed molecules that generates a force on the molecules in a
direction perpendicular to the wall. The energy of wall-particle interactions is set to $30 \frac{kcal}{A^2}$. The second equilibration is for when additional molecules are added to the system. The number of steps in the short equilibration should be scaled according to the number of molecules that are being added into the system. The pair interactions are calculated for the terminal polar bead and the water beads within a radius of 5.5 Å. The number of loops performed for the surface tension measurements according to the test area method is set to 15 and 100,000 equilibration steps are run within each loop. Lastly, the names of the trajectory files (.dcd) can be adjusted to the users preference.

Others that are not included, but may also be adjusted are the time-step, which is set to 2.0 fs, and the number of times the trajectory files are written. A timestep analysis is included in Section A. The user is encouraged to review the LAMMPS documentation for other parameters. The potential cutoff in all cases was 20 Å, approximately $4.5\sigma_{Max}$, suggested for surface tension measurements using the coarse-grained water model. [64, 127, 186, 102]

In step six, seven and eight, the submission file calls on a python script that analyzes the data generated from the compute commands in LAMMPS. The first compute commands chunk/atom and ave/chunk are used to generate the density profiles for the nonpolar, polar and terminal polar beads. The chunk/atom command counts the number of specified beads in 0.25 Å bins along the z-direction and the ave/chunk sums the number of beads in each chunk at each time step, then averages the per-chunk values over the larger timescale. The number of beads is counted every 20 time-steps and the frequency at which averages are taken is variable based on the set the run time. For examples, if the run time is set to 100,000 steps, the number of beads is counted every 20 time-steps, the average of the chunk is calculated every 100,000/20 steps. The radial distribution function (RDF) between the terminal head beads and water groups is computed using
the coord/atom command, which calculates the number water beads within a set radius of the terminal polar beads. For the -CH2OH bead, the radius is set to 5.5Å, which is equivalent to the first hydration shell. The ave/histo command is then used to construct a histogram of the RDF data. The number of water beads in the first, second, third, fourth and fifth hydration shell are printed to a data file that is then used to determine the number of molecules interacting at the interface.

This data file is read in at the end of each run to determine whether enough data has been generated to accurately estimate the maximum surface adsorption. The criteria for determining whether maximum surface adsorption ($\Gamma_{Max}$) is achieved is described in detail in Chapter 5, Section 5.3.4. The first criteria is that the error associated with the polynomial regression curve for the sum of histogram values in the first and second bin versus number of molecules at the surface is greater than 0.90 and the sum of bins is greater than 0.11. These parameters describe whether or not the molecules are interacting at the interface. If the criteria is not met, the number of molecules in the system is increased and the LAMMPS simulation is repeated. Once these criteria have been met, a geometry file is generated with the number of molecules equal to the maximum surface adsorption number ($\Gamma_{Max}$).

In step nine and ten, the geometry file consisting of the number of molecules equal to the maximum surface adsorption concentration are read into LAMMPS using a new LAMMPS input script that performs manipulations on the system to generate data used to calculate the surface tension. The method for calculating the surface tension is described in Chapter 5, Section 5.3.2. During the LAMMPS simulation a python script is called that scales the area of the system and outputs new coordinates which are read back into LAMMPS and used to measure the potential energy of the system before and after the perturbation. The number of times the potential energy of the system is evaluated...
and the number of steps to run prior to the area perturbation are specified in the input file. After the LAMMPS run is completed, the submission script outputs the surface tension of the interface at the set number of molecules.

6.6 Program Execution

To run the program, the initial command is "python src/execute_ADD.py input/structure.txt #", where '#' represents the initial number of molecules to place on each surface and the format of 'structure.txt' is shown in Figure 6.2. The "execute_ADD.py" script calls on the packages PACKMOL and Moltemplate, creates a sub-folder in which all files for LAMMPS runs and post-processing are organized, and calls a script that performs the simulation and analysis loop described in section 6.4, steps 4-10. After submission of the initiating run script, the user will be requested to provide further details on the system to assist in directory organization.

6.7 Analysis

Using the process described in the previous sections, the following output files are generated. The input file in Figure 6.2 and the number of molecules specified by the user are used to generate image (a) in Figure 6.3. Images (b), (c) and (d) illustrate the geometry files after equilibration and density calculations are performed via LAMMPS.

The density data generated using the chunk/atom and ave/chunk compute codes integrated into the LAMMPS input script are used to construct the density profiles shown in Figure 6.4 for 25 (left) and 95 (right) surfactant molecules.

The histogram data generated using the coord/atom and ave/histo compute codes
integrated in the LAMMPS input script is used to construct the histogram plot in Figure 6.5. The plot illustrates the increase in water beads in the first hydration shell of the terminal polar bead as the number of surfactant molecules in the system increases.

In Figure 6.5, the first and second bin depict the number of water beads in the first hydration shell of the terminal polar bead averaged over the time length of the simulation. The sum of these bins is plotted against number of surfactant molecules at the interface and is shown in Figure 6.6 to increase with increasing number of molecules. For surfactants with varying chemistry or topology the user can use the information in the figures above to describe the behavior of the compound at the interface. Another option is to set a standard percentage at which to extract surface tension measurements.

The information in Figure 6.6 is used to determine the number of molecules required for surface saturation. That number of molecules is then used to run an additional simulation during which surface tension information is extracted. The surface tension for the above molecule was taken for 81 molecules, equivalent to 10%, to be 24 mJ/m².

6.8 Impact and Conclusions

In this chapter we introduce a computational tool that can be applied to study interfacial systems. Using AutoSurf, we have studied the behavior of over 500 surfactant/water systems. This tool can be further used to describe surfactant behavior or can be extended to study various interfacial systems, including polymer-mediated surfaces. Additionally, the package can be further developed to use behavioral transformation and structural transformation to implement strategies for generating design variants. This would extend AutoSurf beyond the scope of parametric design into innovative design using search algorithms, such as the Genetic algorithm. Genetic algorithms (GA) are used to imple-
ment operators, such as mutation or crossover, to efficiently search the problem-solution space. Since the goal of computation is to generate many solutions to search chemical space, genetic specification can be used to diverge the search to discover novel desirable compounds.

As an example, a genetic algorithm for surfactant discovery to assist in the replacement of perfluorinated surfactants serves as a motivator for the development of AutoSurf. Perfluorinated surfactants, used in Teflon manufacturing, are environmentally persistent [46, 144] and thus are a major concern for the environmental protection agency (EPA). These surfactants are largely produced along with others, such as AEs, that show up in everyday applications such as shampoo, paint, and detergents. Most of these compounds have gone uncontested since their introduction in the 1960’s. The environmental concern for these commonly used surfactants is low, however, their widespread use suggests that a tool allowing for customization for specific applications would be highly beneficial. The code developed during the investigation of ethoxylated surfactant architecture serves as the foundation for a machine learning tool for the discovery of new surfactants. [154, 178, 1]
Figure 6.3: Illustrations of a surfactant/water system after the initial geometry file is built (a), after LAMMPS equilibration for 1.5 ns of 25 surfactant molecules (b), after LAMMPS equilibration for 1.5 ns of 70 surfactant molecules (c) and after LAMMPS equilibration for 1.5 ns of 95 molecules. The nonpolar units are depicted in teal, polar units in orange, terminal polar in red and water in blue.
Figure 6.4: Density profiles for 25 (left) and 95 (right) surfactant molecules on the water interface.
Figure 6.5: Histogram plot illustrating the number of water beads in the first hydration shell of the terminal polar bead (5.5 Å) for a surfactant-mediated water vapor-liquid interface with 25 surfactant molecules (dark grey), 70 surfactant molecules (light grey) and 95 surfactant molecules (95 molecules).
Figure 6.6: The percentage of molecules with zero or one water beads in the first hydration shell of the terminal head group for increasing number of molecules at the water vapor-liquid interface.
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Appendix A

System Generation

A.1 Surfactant-Mediated Water Vapor-Liquid Interface

Water Slab: The bulk water box had dimensions of 60x 60y 80z and was packed with 4,800 beads. A simulation was run at 298.15 K for 2 ns with a time-step of 1.0 fs to equilibrate the system. An interface was generated by extending the z direction to 3x its original size. A canonical simulation was run for 4-8 ns at the same settings. The test area method and pressure tensor method were used to calculate the surface tension. Both methods gave reasonable surface tensions within 5% of experimental results.

Spline: A cubic spline can be fit to the Mie potential for increments of 0.0005 Å from 1.6 Å to 20 Å. A cubic spline is a flexible numeric function that allows for a high degree of smoothness when curve fitting. This approach minimizes the computational expense of calculating the interactive potential for each bead-bead distance.
**Surfactants:** The surfactants were packed randomly in the vacuum at a concentration specified separately for each system. An energy barrier was implemented at 50 Å from the surface to keep surfactants from migrating to the opposite surface. The system was then allowed to minimize for 3 ns. All simulations were run at 298.15 K with a timestep of 1.0 fs. At the end of the minimization, the surfactants that were not interacting with the surface were trimmed from the system and the system was re-equilibrated for 1 ns. After the system was set up and minimized a final simulation was run for 1.2 ns to calculate system properties. In order to calculate the surface tension using the test-area method an area perturbation was performed every 300 steps and the potential energy from before and after the perturbation was recorded.

### A.1.1 Mechanical Description of Surface Tension

The vapour pressure and the interfacial tensions can be calculated from the components of the pressure tensor. The vapour pressure corresponds to the normal component of the pressure tensor $P^V = P_{zz}$, and the surface tension is obtained from the difference in the normal and tangential components as:

$$
\gamma = \frac{1}{2} (P_{zz} - \frac{1}{2}(P_{xx} + P_{yy}))
$$

where the pre-factor 1/2 is added in cases where two interfaces are present.

### A.1.2 Packing Fraction

The packing fraction provides information on the effectiveness of AE surfactants since the CMC has been associated with the occupation of volume at the interface [1, 117, 118]. A recent paper by Mohamed et. al. introduced the relative surface coverage as a predictive
tool for surfactant performance [117]. In their paper they concluded that a negative linear correlation exists between the packing fraction and surface tension. An illustration of the packing fraction is shown in Figure A.1 and the equation given in Equation A.2

\[ \phi = \frac{V_{cal}}{V_{meas}} \]  

where \( V_{meas} \) is the volume occupied by the surfactant segments and \( V_{cal} \) is the volume that the surfactants occupy on the surface, including free space, \( V_{free} \).

**A.2 Time step Analysis**

An energy conservation test was performed to determine the maximum time step that could be used for the system without inducing large perturbations in the energy. The normalized energy versus the time step is shown in Figure 4. Based on these results, a time-step of 2fs was chosen for all simulations.
A.2.1 Surfactant Table

Table A.1: Surface tension and saturation concentrations for 131 surfactants with varying topologies. The topologies of the surfactants fall into three groups, 2 head beads, 3 head beads, and 4 head beads and are identified as #B#M:#T, i.e. [# branch beads] [# beads in the backbone]: [# beads in the backbone].

<table>
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<tr>
<th>#</th>
<th>2 Head Beads</th>
<th>$\Gamma_{Max}$</th>
<th>$\gamma (mJ/m^2)$</th>
<th>Error (±)</th>
</tr>
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<td>0B:2</td>
<td>99</td>
<td>45.93</td>
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<tr>
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<td>0B:3</td>
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<td>0.69</td>
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<tr>
<td>131</td>
<td>0B:7</td>
<td>79</td>
<td>65.54</td>
<td>0.84</td>
</tr>
</tbody>
</table>

| #  | 3 Head Beads | $\Gamma_{Max}$ | $\gamma (mJ/m^2)$ | Error (±) |

Figure A.2: The normalized energy for a surfactant system using a time step of 1fs (black), 2fs (red), 5fs (green) and 10fs (purple).
Table A.1 continued.

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A.3 AutoSurf source files

The source files for AutoSurf can be located at https://github.com/mjritz/AutoSurf.

A.3.1 GNU Plot

GNU plot is a scientific plotting package that features 2D and 3D plotting, a huge number of output formats, and a large set of scripted examples. The scripts used to generate the plots are included in Appendix A. [145]

To generate the density profiles in Figure 5.20 and 6.4, the following command was used:

```
plot '1_nonpolar.dat' u 2:3 w l, '1_surface.dat' u 2:3 w l, '1_terminal.dat' u 2:3 w l
```

A.3.2 Visual Molecular Dynamics

Visual Molecular Dynamics (VMD) is a molecular visualization program commonly used for displaying, animating, and analyzing large molecular systems. [70]

Data files generated by LAMMPS can be read in to VMD using the following command:

```
topo readlammpsdata *.data full pbc wrap -compound res -all -center origin
```
Appendix B

Slab Construction for *Ab Initio* Calculations

B.1 Silicon Slab Construction

To build the silicon slab the following lattice and symmetry information was used:

1. Chemical formula: Si
2. Space group: 227
3. Crystal system: Face Centered Cubic (fcc)
4. Hermann-Mauguin: Fd-3mS
5. \( a = 5.4306 \) Angstrom
B.2 Virtual Nanolab

Virtual nanolab is a free software for academic users that provides a user-friendly graphical interface that allows for atomic structures to be read in from an integrated database or from previously geometry calculations. Using the imported chemistries, the user is able to assemble a complex systems using the numerous available tools. [172, 159, 168]

Visual Molecular Dynamics (VMD) can also be used in to build bulk slabs. [70].

B.3 Grid and ZTSM

All files used to generate the energy surface in 4.4 and to calculate activation barriers for reactions can be found at:

https://github.com/mjritz/GridDFT

B.3.1 GNU Plot

GNU plot is a scientific plotting package that features 2D and 3D plotting, a huge number of output formats, and a large set of scripted examples. [145]

To construct the energy map in Figure 4.4, the following commands were used for a 4 by 4 grid:

    set yrange [0:5] set xrange [0:5] set cbrange [0.15:-0.15] set palette maxcolors 15 splot 'surface_plot' using 1:2:3 with points pointtype 5 pointsize 9 palette linewidth 30