ADSorption and Surface Structure Characteristics
Toward Polymeric Bottle-Brush Surfaces Via Multiscale Simulation

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ABSTRACT

For decades, device design has focused on decreasing length scales. In computer and electronic engineering, small feature sizes allow increasing computational power in ever-smaller packages; in medicine, nanoscale in vivo devices and sensors and coatings have myriad applications. These applications all focus strongly on material/component interfaces. While recent advances in experimental techniques probing interfaces at nanometer and sub-nanometer scales have improved dramatically, computational simulation remains vital to obtaining detailed information about structure and energetics in nanometer-scale interactions at interfaces and the physical properties arising from interactions at larger scales.

We start with all-atom molecular dynamics simulations of methane and chloromethane adsorption on the (100) surface of molybdenum to understand adsorbate polarity/geometry and substrate interaction potential effects on interfacial structure, packing and energetics. For featureless substrates, adsorbate geometry and orientation do not influence packing and affinity. Substrates with explicit surface structure show cooperation between substrate and adsorbate geometry via adsorption-site preference. Methane prefers sites over unit cell faces, roughly commensurate with the Mo surface, whereas chloromethane invites disorder, orienting its long axis along “bridges” between surface Mo atoms.
In the second phase, we used a coarse-grained bead-spring model to perform simulations of bottle-brush homopolymers tethered to a wall substrate at long time/length scales. We studied the intra- and intermolecular accumulation of tension in tethered bottle-brush backbones vs. bottle-brush dimensions and surface grafting density. Variations in bond force and bottle-brush/component shape and size descriptors uncovered three tension "regimes": (i) an isolated-brush regime (low surface grafting density), where intramolecular interactions dominate and tension is minimal; (ii) a "soft-contact" regime, where neighboring bottle-brushes' side chains overlap, compressing side chains and transmitting moderate tension to backbones; and (iii) a "hard-contact" regime, where increased side-chain overlap forces reorientation, accumulating significant backbone tension. We then performed a small number of simulations of tethered bottle-brushes with two different side chain types to illustrate the morphologies available as a result of microphase separation, varying the strength of the interactions between side chain types. Continuing this work in the future should help discover other possible applications arising from varying the chemical nature of the side chains.
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CHAPTER I
INTRODUCTION

Advances in modern technology are fueled by miniaturization. Advances in lithography have placed a seemingly ever-increasing amount of components into integrated circuits, pushing computing power that once dominated buildings into telephones and personal accessories that can be lost in the hands of careless users. The drive to smaller, more specialized devices and molecules has also given birth to revolutions in medicine: treatments for cancer and other diseases that once involved often toxic agents whose effects were simply accepted and mitigated can be alleviated by ligand-decorated nanoparticles modified to express specific interactions and deliver therapeutic agents directly to affected cells, while biological nanosensors used to isolate and interact with specific pathogens, proteins and even specific peptides via interaction with functionalized surfaces offer a novel alternative to costly, time-consuming laboratory analysis. In each application, though, it is surface functionalization and control of interfacial interactions that drives the rational design of nanoscale devices; a revolution in device miniaturization is in many ways a revolution in our understanding of interfaces.

In recent years, considerable interest has surrounded the use of functionalized oligomeric/polymeric substrates in such nanoscale devices. As we well know, polymers are extremely versatile — by changing the architecture and/or molecular size and shape, altering the chemistry of the end groups, including charged or...
conductive groups at specific areas within the polymer and creating multiblock co-
polymers which can phase-separate into a number of different morphologies, one
 can use the tools of synthetic chemistry to tailor a polymeric surface to express
specific chemical behavior while creating an altogether different structure and char-
acter beneath the surface, introducing multiple elements of design specificity into
a single device surface. From uses of self-assembled monolayers (SAMs) in organic
transistors[1, 2] and chemical sensors[3, 4] to dense, shape-changing pH-responsive
polymer brushes on surfaces used as gates for ion and particle transport[5] or in
selective ion sequestration/exclusion[6], oligomer- or polymer-functionalized sur-
faces are taking advantage of structure and chemistry at the molecular level, both
at the limit of interfaces and within interfacial regions, to create a vast space of
possible applications.

With such a colossal number of parameters to control and interactions to
keep in mind, then, the key to rational device design is in our own understanding
of molecular-level structure, dynamics and interactions between components at in-
terfaces and molecules on surfaces. Experimental characterization of surfaces has
advanced greatly in recent decades and offers many promising avenues for future
developments, although each arrives with its own set of advantages and disad-
vantages. Electron microscopy techniques often used to generate detailed images
of surface structures often require sample fixation for ultra-high vacuum environ-
ments, which precludes most studies of liquid/solid interfaces; in addition, while
such images are useful for detailing surface structure, they offer little to nothing for
evaluating the chemical environment at interfaces. Spectroscopic methods, from
Fourier Transform Infrared spectroscopy (FTIR spectroscopy) to Raman spec-
troscopy to sum-frequency generation (SFG) spectroscopy, offer chemically-specific information as well as information on structure and orientation of interfacial components. Of these, basic IR spectroscopy tends to lack surface specificity, Raman spectroscopy (and the variations of surface-enhanced and tip-enhanced Raman spectroscopy) can give detailed chemical, structural and orientational information at interfaces, but largely employ substrates or AFM tips specially treated with gold or silver to enhance the signal. SFG spectroscopy may be the best option for characterizing liquid/solid interfaces, combining high-level chemical specificity with the ability to collect structural and orientational information even at somewhat buried interfaces; SFG is sensitive to non-centrosymmetric media, thus avoiding bulk contributions and focusing on interfaces. Femtosecond-pulse SFG can also be used to probe dynamics at interfaces, which is much more difficult with other methods. As advantageous as it has been, however, SFG also has its own limitations: typically, the tunable IR portion of the setup controls the usable range of probing frequencies, extracting detailed orientational information can be highly geometry-dependent and difficult to extract from direct SFG experiments, and high laser intensities carry the possibility of causing damage the target surfaces[7].

As a complement to experimental methods, computational simulations are an invaluable tool for the examination of interfaces and surfaces. Multiscale simulations in particular offer the ability to focus attention on specific time and length scales for specific interactions or physical properties. Quantum simulations of small atomic and molecular systems are often used to determine preferential structure, electronic charge distributions and can be used in comparison with experimental techniques such as vibrational spectroscopy, with accurate simulations
used to understand the modes that give rise to specific vibrations. Information gained from *ab initio* quantum chemistry simulations is often used in the creation of empirical force fields such as those used in all-atom classical simulations. All-atom force fields derived from first principles calculations are then well-suited to the study of structure, packing, orientation and dynamics of atoms and molecules as well as the energetics of specific-site interactions such as hydrogen bonding or substrate-adsorbate interactions. The first phase of our simulation study begins at this level. Using well-known and verified empirical force fields, all-atom molecular dynamics simulations of simplified systems — methane and chloromethane adsorbing on a well-defined molybdenum surface — were used to study how differences in adsorbate chemistry and geometry and the modeling potential for the substrate surface could change the structure and binding energy between alkanes. In this case, alkanes are a particularly interesting basis for studying the structure and energetics of adsorption as a first step in understanding how more complex molecules’ end groups would interact with such surfaces, and how the orientation, packing of such end groups might affect the structure of adsorbed hydrocarbons or organic macromolecules.

While such models provide essential insight into the fundamental physics that guides surface adsorption and interfacial structure, current trends in device design favor the use of more complex surfaces, such as those provided by polymeric substrates. From self-assembled monolayers functionalized with a wide variety of tail groups to linear brushes of multiblock copolymers, polymeric surfaces are able to take advantage of both chemical effects and functionalization as well as architectural effects that can be used to present the desired chemical functionalities.
to interfaces with a considerable degree of control. One particular polymer architecture — the bottle-brush polymer — was the focus of the second phase of our investigations. Recent advances in synthetic control have made this relative of the comb polymer attractive in a number of applications, due to the ability to tailor the side chains by including different chemistries[8–13] and architectures[14, 15] at different points along the backbone. The high density of side chains, the steric repulsion responsible for the extended backbone conformation/overall molecular shape, and the apparent lack of entanglement between side chains[16] present a unique template for applications.

Free bottle-brush systems have seen uses as highly controllable nanopatterns on surfaces[11], in nanocapsules for separation/sequestration in liquid mixtures[17] and as templates for the synthesis of nanowires and nanoclusters[18]. Bottle-brush polymers tethered to a substrate, on the other hand, become a complex surface that can be loaded with multiple chemical species to exploit side chain and backbone structure; applications range from nanoparticle functionalization for drug delivery[19] to detailed photoresist layers[8] to surfaces that selectively adsorb/repel biological materials[20–22]. Even with this number of applications, however, much remains to be understood about the character of surfaces created by bottle-brush tethered layers. In particular, it has been discovered that the side chains of bottle-brush polymers in contact with an attractive substrate spread along the surface to maximize contact and that this spreading of side chains is responsible for the generation of tension within the brush backbone, in some cases enough to cause backbone and/or side chain bond scission[23–26]. The sizes of such macromolecules and the time scales of structural rearrangement, with the
concomitant effects on surface surface structure and adsorption, unfortunately remove simulation of such bottle-brush systems from the range accessible by all-atom simulations. In such situations, an abstraction to a coarse-grained model is necessary to access simulation time scales that often range from nanoseconds to milliseconds and length scales that range from nanometers to microns and above.

Our original proposition for the current study was to use such coarse-grained models to simulate the interaction between adsorbates of different character, from small molecules to possibly peptides and whole proteins, and the surface of dense layers of bottle-brush polymers tethered to an ideal surface, such that the interface of interest is the free surface of the brush. Early into the research process for this investigation, however, it quickly became clear that not only was adsorption of other species onto a densely grafted bottle-brush surface lacking, but a clear characterization of the structure of such densely grafted bottle-brush layers was also missing. Thus, we shifted our attention to that problem, using coarse-grained simulation to better understand the relationships between the size (controlled by degree of polymerization of the backbone and side chains) of homopolymer bottle-brush molecules, the density of grafting at an ideal nonadsorbing surface, and the accumulation of tension and rearrangement of side chains as a result of size and crowding effects. In this way, we have attempted to set the stage for future investigations of the surface character of bottle-brush tethered layers by first characterizing the structure that arises from the packing imposed on backbones and side chains by both intramolecular and intermolecular interactions. Our goal in this investigation is then to lay the underpinnings for a more comprehensive theory of the structure inherent in dense bottle-brush tethered layers as well as
to outline the challenges that accompany the development of such a theory in which the overall behavior and applications of these materials are governed by a parameter space much larger than any one investigation can explore.

The remainder of this work is outlined thus: in Chapter 2, we start by detailing a short literature review related to central concepts in adsorption, both for polymers and small molecules, and the applications and uses of simulation in the study of those systems. We also discuss briefly some of the types of simulations available and their uses, setting the stage for the specific methods used in this study.

In Chapter 3 we begin the discussion of the simulation results by examining all-atom simulations of a simplified system: small-molecule (methane and chloromethane) adsorption on a flat, featureless Lennard-Jones wall and on the (100) surface of molybdenum, itself treated via three different molecular dynamics potentials, to highlight some of the challenges regarding the simulation even of such basic systems. The focus of this portion of the study is to examine how the changes in surface potential and changes such as the replacement of a methane hydrogen with a chlorine atom alter the structure, orientation, packing and energetics of adsorption at surfaces of similar construction modeled independently. Beyond the central purpose in this section, this part of the study also highlights some of the challenges with the choice of force field in detailed all-atom simulations and the effects that can arise from subtle changes in simulation parameters.

In Chapter 4 we move to the direct simulation of our system of interest — tethered layers of homopolymer bottle-brush molecules — employing coarse-grained molecular dynamics simulations to study how altering the size of the
primary components of the bottle-brushes, the side chain and backbone lengths, as well as the degree of surface crowding, induced by altering the surface grafting density of the physically (not covalently) tethered bottle-brush molecules, affect the structure of the bottle-brush molecules and their components, how this affects the organization and orientation of side chains as surface grafting density forces more and more bottle-brush molecules into one another, how the nature of the bottle-brush side chain interactions and the effects of this surface crowding elicit the accumulation of tension within the bottle-brushes and the layer as a whole, and the implications for this tension accumulation in possible applications of molecules with the ability to self-generate tension wholly through architectural effects, long before chemical interactions are introduced into such a system.

In Chapter 5 we examine the possibilities suggested by including different chemical species in the side chains by examining block brush copolymers, similar to those suggested in work by Grubbs, et al., tethered to a surface in order to see how phase separation of such tethered molecules can lead to interesting and varied layer morphologies, control over which is suggested to be part of a highly complex parameter space that we can only suggest at this time. Following this, we summarize the conclusions for all of the simulations posed in Chapter 6 and suggest a future outlook for extensions that could carry this work in a number of substantive directions.
2.1 Small-Molecule Adsorption: Structure, Dynamics and Energetics

Small-molecule adsorption on solid substrates has been a topic of interest for many decades. Early work in the 20th century focused on descriptions of adsorption of gas molecules onto solids (but has been used since in terms of liquid/solid adsorption with some adaptation) in terms of the coverage, or amount of adsorbate that could readily adsorb onto a surface of a given character. Work done on the development of adsorption isotherms to adequately model such adsorption resulted in the well-known Langmuir\cite{27, 28} and Freundlich\cite{29} isotherms, the former of which was extended from its central idea of monolayer adsorption to multilayer adsorption in BET theory\cite{30}, which is still commonly used today in the measurement of the specific surface areas of porous media.

In the 1960s and 1970s, questions began to arise regarding the nature of phase transitions, especially the melting transition, in physisorbed layers across a variety of substrates, most commonly noble metals or graphite. Rare gases and other "closed-shell" molecules have often been used as the adsorbates in such studies, as the lack of reactivity of such species with the surfaces of interest or the ease with which one can identify the adsorbate-adsorbate and/or adsorbate-substrate interactions, creates near-ideal model systems for experimental focus. Interest in the nature of physisorption appears to have spiked around the time that
low-energy electron diffraction became a more popular tool for the study of the structures of adsorbed layers on crystal surfaces in the early to mid-1960s\cite{31–33}; numerous other studies followed as it became clear that diffraction techniques such as LEED\cite{34–37} and X-ray diffraction\cite{38–42} could be used to obtain sufficient structural and orientational information to construct reliable monolayer phase diagrams.

In the early 1970s and thereafter, interest in monolayer and submonolayer adsorption was piqued by the development of the Kosterlitz-Thouless-Halperin-Nelson-Young (KTHNY) theory for two-dimensional phase transitions (extending the previous work of Kosterlitz and Thouless on the 2D XY model)\cite{43–47}. Sub-monolayer and monolayer systems of adsorbed rare gas or closed-shell molecules are essentially two-dimensional on top of the substrate and thus make an excellent model for testing the theory by observing the changes in layer structure with varied temperature as a function of the coverage at the surface. According to the theory, the melting transition in two-dimensional systems follows a far different behavior than three-dimensional systems. In two-dimensional crystalline solids, translational order is quasi-long-range, instead of truly long-range in the case of three-dimensional solids, and the first part of the melting transition occurs with the introduction and unbinding of dislocations within the structure. The production of such dislocations destroys the normal six-fold symmetry and marks the transition from the solid phase to the \textit{hexatic} phase, an intermediate phase in which the quasi-long-range translational order is lost, although long-range orientational order is maintained. At a higher temperature, a second transition takes place in which the long-range orientational order is lost and the hexatic phase
transitions to the isotropic liquid. Both transitions are expected to be continuous, unlike the first-order phase transitions that occur in three-dimensional solids[48].

Verification of KTHNY-type behavior in experiment and simulation has, traditionally, been more difficult to come by. In rare gas systems on graphite, it has been noted that most systems suggest show first-order melting transitions, especially below monolayer coverage[39, 49, 50]. Close to or above monolayer coverage, however, the evidence is slightly more contradictory. While a number of x-ray diffraction studies[39, 51, 52] suggest either continuous phase transitions or a progression from first-order to continuous at higher coverages in xenon on graphite, a heat capacity study by Jin, et. al.[50] confidently claims the melting transition for Xe on graphite at monolayer coverage is always first-order. In contrast, in a heat capacity study of argon adsorption on graphite, Migone, et. al.[53] described a "weakly first order" transition in terms of a single sharp peak followed by a broad peak described as a loss of six-fold symmetry, while simulation work by Flenner and Etters[49] suggests that these peaks may actually be the signature of the two-part continuous melting transition from solid to hexatic fluid to isotropic fluid. Thus, even in simplified systems such as rare gases on graphite, the phase behavior and changes in structure upon temperature variation are not well understood.

The situation becomes slightly more complicated, but also more concrete in application, when the adsorbate changes to small hydrocarbons such as methane or various halomethanes. For methane or perfluoromethane, the structure and behavior might be expected to be similar to that of the rare gas adsorption studies, as the symmetry of the CH\textsubscript{4} and CF\textsubscript{4} molecules makes them behave more like the rare gases, particularly for CF\textsubscript{4}, for which the strong C-F interaction makes the
overall molecule moderately less reactive. Notable differences are still present, however, as the CF$_4$ molecule is substantially larger than many of their rare-gas counterparts, and the geometry of the molecule is thought to favor different adsorption sites\cite{40}, thus these molecules present a similar yet nuanced basis for the study of the structure of films upon adsorption. More than the fundamental understanding, however, methane and halomethane adsorption has been renewed in recent years due to the development of novel materials particularly well suited to the treatment and storage of gases, methane in particular as the main component of natural gas, which has been explored as an energy source that may help meet our needs in the transition to cleaner alternatives. While natural gas is currently used in a number of niche applications, issues with storage and specifically with storage media that can attain high energy density without having to rely on low-temperature liquefaction or compression at very high pressures are envisioned to assist tremendously with expanding the reach of this fuel.

Computer simulations of physical adsorption have come into a place of prominence in recent decades for their ability to portray adsorption at a molecular level and, alongside experimental techniques such as neutron scattering, have proven a valuable asset for research regarding the structure and orientation of adsorbed layers of molecules on solid substrates. From simulations regarding the fundamental structure and thermodynamics of adsorbed alkanes and alkane derivatives on graphite\cite{54–56} to simulations regarding porous substrates such as zeolites\cite{57–61} for applications ranging from heterogeneous catalysis to gas or liquid filtering, sequestration and storage, computer simulation has been used quite extensively to study various aspects of physical adsorption.
In recent years, a large segment of focus in adsorption research, and simulations in particular, has shifted toward problems in biology and biochemistry, namely the adsorption of peptides, sequences of peptides and even full proteins on a number of different surfaces. The reasons to study peptide/protein adsorption on a wide array of surfaces has much to do with possible intended applications — recent studies regarding the characteristics of peptide adsorption on noble-metal surfaces[62–64] have used the electrochemical properties of these metals to study not only the peptide/inorganic interface, but also to probe the capability of using noble-metal devices in sensory and medical diagnostic applications. At the same time, simulations in the peptide/protein arena have also been probing interfaces between peptides and metal-oxides or mineral frameworks[65–68], often with an eye to understanding the binding processes that may underlie fundamental aspects of biomaterial compatibility with living systems.

Many such simulations examine the interaction between the adsorbate and substrate with high degrees of detail, which can be difficult to model feasibly even by today’s computing standards. All-atomistic representations of complex molecules and increasingly detailed force fields for governing interactions with different surfaces have amplified the applicability and feasibility of computer modeling to engage some of the more traditionally intractable problems in surface science. However, often it seems that these studies deal only with one side of the adsorption problem — the adsorbate — by focusing on the specific peptides and peptide sequences that bond preferentially to a surface. What we propose, in this study, is to investigate what effect changes in the substrate structure can enforce on adsorbate binding, structure and orientation and question whether or
not such changes can be significant to understanding the overall mechanism of physical adsorption.

To that end, our study focuses on a highly simplified series of systems, structured around adsorption of methane and chloromethane on the (100) surface of molybdenum, a metal exhibiting a body-centered cubic structure, with the difference in adsorbate designed to probe the effect of adsorbate polarity on the choice of adsorption sites and the induced orientation. Molybdenum is a particularly interesting substrate both because it is seemingly used less often in research — and simulations such as those that follow, especially — than its noble-metal counterparts. Molybdenum itself, however, has been argued[69] to be an efficient substrate to catalyze the breaking of carbon-carbon bonds, especially in small-chain alkanes, while oxides of molybdenum, in concert with certain zeolites, have been shown to have notable affinity for methane and small-chain alkanes in processes for the synthesis of larger groups[70]. Thus, it appears that molybdenum and similar transition metals may share an affinity for small alkanes that may not be shared by their more commonly seen noble-metal cousins.

Thus motivated, we seek to test the forms of potentials used to govern the molybdenum substrate and the mobility of the substrate, introducing vibrational freedom in atomic positions near the metal-liquid interface in order to see if such changes can elicit notable changes in substrate surface structure and thereby enforce changes in interfacial adsorption with the targeted alkanes. We do this by examining structural and orientational properties of the adsorbed layers closest to the substrate surface to determine how they react to different surfaces, and we also estimate the binding energy between the simple molecules at different sites on
the substrate surface to see whether certain sites on differently modeled substrates provide differences in the strength of attachment to the surface.

2.2 Tethered Bottle-Brush Layers: Structure and Tension Accumulation

Bottle-brush polymers and comb-like polymers in general have long attracted significant attention in both academic research and industrial applications and have been prolific in applications in nature. The basic form of a comb-like polymer combines two principal components: a central linear backbone and multiple linear “side chains” grafted to it. Varied together or independently, the physical structures and chemical compositions of these components create a highly versatile framework for a number of applications. This versatility is already apparent in nature from comb-like versicans, acting on cell proliferation and adhesion[71, 72], to the surface of human lung tissue where, when well-hydrated, the bottle-brush structure of the PCL acts as an osmotic barrier to penetration by mucus and foreign particulates, facilitating airway clearance[73]. Perhaps best-known of the bottle-brush macromolecules found in nature, however, are aggrecans, which are critical to the structure and function of articular cartilage[74–76]. Aggrecans have been studied extensively in recent years, from both experimental and theoretical perspectives[77–83], in order to understand how they provide such a low coefficient of friction to synovial joints as well as how these properties can be replicated synthetically.

The primary factor separating bottle-brush polymers from the more general comb polymer is the grafting density of side chains along the backbone. In comb polymers, this grafting density is low enough that backbone flexibility is
largely unaffected by the presence of side chains. As side-chain grafting density increases, the distance between adjacent side chains along the backbone becomes smaller than side chain lengths themselves, and steric repulsion between side chains begins to overwhelm the conformational entropy of the backbones, resulting in backbone stretching[84, 85]. The amount of stretching itself depends on the dimensions of the side chains, the grafting density, and interactions with the backbones.

Studies of bottle-brush polymers have thus far focused primarily on their structure, conformations in specific environments and self-assembly behavior in brushes with multiple side-chain types or chemical compositions. Grubbs and co-workers used a ring-opening metathesis polymerization to create macromonomers of various linear polymers with norbornene end groups in the synthesis bottle-brushes with multiple side-chain types tethered to a polynorbornene backbone. Their previous work suggests that the lamellar structures from self-assembly of brush copolymers with two types of side chains can be controlled by changing the arrangement of the side chains or by altering the degree of polymerization of the backbones or side chains[12, 13]. Later work suggests that these brush block copolymers can be exploited in applications for nanopatterning surfaces[11]. Block brush copolymers are also capable of forming multi-component nanocapsules[17] and core-shell cylindrical brushes[9, 10], with structures in the latter case having applications in the fabrication of nanowires[18] and wire-shaped nanoparticle assemblies[86]. Multi-component brushes also mark a synthetic route to Janus particles or Janus-type polymers, which have been a target of increasing study both from synthesis and simulation[84, 87–93].
Perhaps the best-known role of tethered bottle-brush molecules or bottle-brush structures comes from biological applications, among the most well-known of which are proteoglycan bottle-brushes known as *aggrecans* that form one component of the surface of articular cartilage. Composed of a protein core itself attached at one end to hyaluronan chains and to which highly charged chondroitin sulfate side chains are densely grafted, it is thought that the large negative charge density imparted by the side chains is critical to maintaining a high degree of hydration in the articular cartilage surface. This hydration and the brush structure itself combine to help explain the low coefficient of friction and high strength of these natural surfaces and have been used to attempt to synthesize such surfaces for medical applications. Work on the characterization of synovial joint lubrication by Klein and co-workers[74–76] has led to important extensions in both theory and experiment[77–83] regarding the physical properties of polyelectrolyte bottle-brushes under opposing pressure and shear stress.

In addition, recent research on the structure of the periciliary layer (PCL) of airway epithelial shows the importance of the bottle-brush structure in the clearance of mucus. In this work, it was shown that large mucin macromolecules tethered to surfaces of motile cilia behave much like a tethered layer of bottle-brush molecules and that this dense layer structure is effective in lowering the permeability of the PCL by large molecules such as mucus chains or particulate matter. Under normal conditions or increased hydration, this results in a strong PCL that rejects foreign matter and creates a distinct two-layer system in which the mucus layer rides atop and is cleared more easily by the PCL. At the same time, this model also helps to explain how PCL dehydration results in immobilization of
the cilia, which is related to the pathogenesis of diseases such as cystic fibrosis and chronic obstructive pulmonary disease[73]. Bottle-brush applications are also important in the design of biological devices, such as those involving surfaces that resist fouling by certain classes of molecules or biomolecules. Dense tethered layers of poly(oligoethylene glycol) bottle-brushes have already been shown to exhibit remarkable resistance to protein adsorption[21, 94–96] and can be altered, by manipulating grafting density and component dimensions, to create porous surfaces capable of transporting or trapping non-protein molecules via size exclusion[97]. Other functionalized surfaces with this type of chemistry have been used in applications from support for protein arrays[20, 98] to surfaces that improve the acceptance of biometallic implants[99] to waste-water remediation via brush-functionalized magnetic nanoparticles[100]. Synthesis of dense layers of surface-tethered bottle-brush molecules remains a topic of significant interest in chemistry as methods used previously, such as surface-initiated atom transfer radical polymerization (SI-ATRP)[101–103] and iniferter-based photopolymerization[104, 105], are useful for creating surface-tethered branched or even hyperbranched molecules but remain limited with regard to surface grafting density or growth of side chains. More recent work[106] suggests a route for high control of surface grafting sites using plasma deposition of ATRP initiator sites, although such methods may still experience problems related to side-chain growth in environments with a high grafting density of backbone polymers.

Device design in contemporary materials science has built on such studies of structure and chemical or physical behavior to elicit a number of potential applications from the exercise of molecular-level control. From actuators based vari-
ations in solvent quality or pH to highly ordered structures such as self-assembled monolayers, taking advantage of strong non-bonded interactions to create well-defined and controllable structures, understanding the effects that control the physical properties of polymers, segments of polymers or even specific groups within polymers is key to understanding how best we can use novel polymer architectures to generate applications. Recently, it was demonstrated that the steric repulsion between side chains that restricts backbone conformations also transmits significant tension from the side chains to the backbone\cite{23–25, 107, 108}. This tension can be amplified by enhancing the crowdedness of side chains by tethering the backbone to a substrate or by allowing adhesion of the side chains to an attractive substrate. Using such approaches, it may be possible to engineer applications of bottle-brush polymers to take advantage of such tension-generating behavior, to create self-modifying surfaces or to elicit specific reactions in response to stimuli in order to express different chemical groups or physical structures at interfaces.

In a series of scaling analyses, Panyukov et al., examined the connections between backbone tension amplification and polymer conformations for branched polymers such as stars and pom-poms\cite{109}, bottle-brushes in solution and adsorbed on surfaces\cite{110} and star and bottle-brush polymers tethered to surfaces\cite{111}, the latter two providing the starting point of the current investigation. In those works, the authors discussed the importance of the two primary length scales in individual bottle-brushes: $D$, the cross-section diameter of the brush as determined by the equilibrium conformations of the side chains (in the analysis of tethered bottle-brushes, $R$ was used as the diameter of the bottle-brush molecule; we will use $D$ here), and $L$, the contour length of the backbone, which
is dependent on intramolecular steric repulsion. In general, bottle-brush behavior can be divided into two key classes based on the values of $D$ and $L$: "hairy" bottle-brushes ($D \gg L$), which are comparable to star polymers and exhibit progressively increasing tension as a function of distance from the backbone free end, and "crew-cut" bottle-brushes ($D \ll L$), cylindrical molecules that exhibit tension increase only within the end-cap region near the free end(s).

Tethering bottle-brush polymers to a substrate introduces a third important length scale: the molecular coverage ($\Sigma$), representing the number of bottle-brush molecules per unit of surface area (the distance between nearest-neighbor tethering sites, $d$, gives an equivalent measure of grafting density, but makes for a more facile comparison with the length scales of the bottle-brush molecules themselves). If bottle-brushes are sparsely grafted to a substrate, the inter-brush distance remains larger than the lateral size of the brushes and intramolecular interactions dominate the self-generation of tension within the brush, independent of $\Sigma$ but affected by the side-chain grafting density and/or the side-chain length. However, as $\Sigma$ increases and the inter-brush spacing becomes less than the diameter of the bottle-brushes, side-chains of neighboring bottle-brushes overlap, causing additional tension accumulation in the backbone. If the amount of overlap is sufficient to perturb the structure of the side chains near the bottle-brush core, this accumulation of tension increases dramatically, and may be enough to break bonds within the backbones. In the current study, we use coarse-grained molecular dynamics simulations to monitor the changes in side-chain conformation as overlap is introduced and increased and to understand how changes in side-chain
conformations at different molecular coverages are reflected in the amplification and accumulation of tension in the bottle-brush backbones.

Previous computational simulations of bottle-brush polymer systems can generally be divided into two categories: bottle-brush polymers with limited side-chain lengths \((N_{sc} \leq 50)\)\[89, 93, 112\] in the study of brush conformations for a small number of chains or for systems using periodic boundary conditions in one direction to simulate single bottle-brush polymers with an effectively infinite, rigid backbone for the study of conformations of long side chains\[88, 90, 92, 113\]. The current work sets out to study multiple bottle-brushes with a significant density of moderately long side chains (50-200 units) grafted to backbones with lengths from 50-200 monomeric units in order to examine a broader class of bottle-brush polymers. To the best of our knowledge, this represents the first simulation study directed toward refining and complementing the existing theory regarding tension accumulation in dense bottle-brush tethered layers while offering more detailed information regarding the changes in chain conformations that give rise to backbone tension accumulation and amplification.

2.3 Brief Background on Computational Simulation

The choice of methodology for any problem in computational simulation centers on the answers to several questions, most notably regarding the time scale of the behavior being investigated and the length scale (or size, in number of particles) of the system of interest. If computational resources and time were no issue, it would be best to start at the level of quantum mechanics via \textit{ab initio} simulations, which focus on electrons — electron density, electronic band struc-
ture, bond energy and preferred conformations, etc. — by attempting to solve the many-body electronic Schrödinger equation. Solutions to such a problem are difficult at best. Full configuration interaction methods are theoretically capable of arriving at exact solutions for the electronic wavefunctions, but the computational complexity scales factorially with the number of electrons and the size of the basis set used. In such cases, solutions are computationally feasible only for systems containing on the order of 10 electrons and using relatively small basis sets[114]. For larger systems, a wide range of approximate methods, from coupled-cluster to the most basic Hartree-Fock, show exponential scaling with the number of electrons, N (on the order of N\(^7\) for CCSD(T) to N\(^4\) or less in certain cases of Hartree-Fock methods), as do methods based on density functional theory (often quoted as N\(^3\))[115]. Overall, however, even the most efficient of these methods show scaling that traditionally limits system sizes to a few hundred atoms.

For macromolecular simulations, simulations of large numbers of small molecules, simulations of large-scale surfaces or any combinations therein, reasonable system sizes in the thousands to tens of thousands of atoms mean that most quantum approaches are best used for the creation and verification of classical simulation methods.

One of the key simplifications that makes several quantum methods viable for simulations is also used as a basic assumption of classical simulation methods: the Born-Oppenheimer approximation[116]. In its most basic form, it suggests that the wavefunctions of the nuclei and the electrons of materials can be decoupled from one another, as nuclear motion is expected to take such time that the electrons have sufficient time to relax to their instantaneous ground state config-

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uration, and thus experience the nuclei as if they were fixed in space. In quantum systems, this is used to justify the primacy of the electronic wavefunction — the motion of the nuclei, in the electron frame, is so slight that the total kinetic energy becomes negligible and the potential energy of the equilibrium configuration can be treated as a background field for the electronic degrees of freedom. Classical simulation methods take the opposite viewpoint, focusing on the nuclei and treating the electrons as a sort of ”spread-out” and separate entity, which is often not treated explicitly. Classical simulation then goes further to assume that the heavy nuclei can be thought of as classical particles which follow Newtonian dynamics.

At the atomic and molecular levels, computational simulations can be broadly divided into two main methods: Monte Carlo (MC) methods and molecular dynamics (MD) methods. Monte Carlo methods are stochastic; in basic Metropolis Monte Carlo, random displacements from a given configuration of a simulation system are evaluated in the context of a total potential energy function representing the sum of all relevant interparticle interactions, such as van der Waals and Coulomb interactions between non-bonded entities and bond, angle and torsion interactions between bonded components. In a given iteration of the algorithm, displacements that result in a net decrease in energy are statistically more probable and are maintained to the next iteration; displacements resulting in an energy increase are accepted with a probability based on the statistical likelihood of such a transition taking place. In this way, unfavorable moves that may lead to a more favorable configuration in the future are not immediately discarded, but are explored with a probability based on the actual statistical probability of the system entering such a state. Over a number of iterations of the algorithm, the
system explores the phase space available, and as the system visits specific config-
urations, a probability distribution of such states emerges which can be used to evaluate average thermodynamic quantities of interest from the distributions obtained.[117]

The simplest Monte Carlo algorithms have traditionally been carried out on a lattice, making trial moves discrete transitions between possible configurations, and trial moves are often taken from a predetermined set of allowed moves. In this way, the MC algorithm becomes a computationally efficient method of exploring the phase space available to a given system and is often used to find the most likely equilibrium structure of a given simulation system. Traditionally, the downside of Monte Carlo simulation are related to the lattice and the often static nature of the algorithm. In the case of the former, a significant number of lattice sites must be left empty in order for trial moves not to result in unfeasible overlaps; this limits such simulations to relatively low densities. In addition, a fixed lattice requires that such simulations be performed under constant volume conditions. Additionally, the algorithm is not intrinsically linked to the dynamics of the given simulation system; the trial moves made during a Monte Carlo simulation do not necessarily represent the way in which a simulation system would evolve in time due to the interactions of freely moving particles, atoms or molecules. Methods such as Kinetic Monte Carlo have been developed which can recover the time evolution of the simulation systems, but for many simulations in which the evolution of the system under observation is desired, molecular dynamics methods offer not only direct and facile access to structural information in simulation systems in an off-lattice basis that avoids the low-density and constant-volume restrictions on
traditional MC but also time-dependent motion based on the instantaneous interactions present in a given simulation system. For our purposes — studying the paths small-molecule adsorbates take through time to adsorb on metal interfaces and the generation and accumulation of tension in dense and dynamic systems of tethered polymer bottle-brushes — molecular dynamics simulation offers clear advantages over traditional Monte Carlo methods.

2.3.1 Basics of Molecular Dynamics Simulations

The heart of molecular dynamics simulation lies in the calculation of the forces on constituent particles due to their interactions with other particles in the simulation environment. As a classical simulation method, this means that the basic equations of motion underlying MD simulations are Newtonian:

\[ m_i \ddot{r}_i = f_i = \frac{\partial}{\partial r_i} U(r^N) \]  

(2.1)

Here, the potential energy \( U(r^N) \) is a function of the particle coordinates and represents the sum of potential energy terms arising from each of the relevant interparticle interactions under consideration. Molecular dynamics simulation then reduces to nothing more than solving this equation by integration of the equations of motion to determine the position and velocity of each of the simulation particles as a function of time. The complexity of the integration depends on the specific form of the potential energy function \( U \).

Although molecular dynamics simulations deal explicitly with the time evolution of the simulation systems they treat, numerical integration requires a discretization of time, with integrations of the equations of motion performed in
units of this discrete "step", known as the time step. The choice of time step is critical, as it is intimately related to and essentially chooses the time and length scales accessible to the specific simulation. Computational time is in part related to the number of position/velocity/energy updates needed for each of the particles in the simulation system, thus choosing an integration time step 10 times larger for one simulation than another should, in theory, allow for that simulation to reach time scales 10 times as long, and one generally wishes to choose the longest time step that the level of simulation detail will allow.

Clearly, though, one cannot choose the time step to be arbitrarily long. If one is interested in MD simulation that accurately predicts the motion of atomic systems, a time step longer than the period of the fastest atomic motion in the system will fail to accurately capture the dynamics associated with those particles. The time step then helps to define the level of detail of the simulation as well as the accessible time scale; e.g., to perform a simulation of a polymeric system with full atomistic resolution, the fastest motion in the system is generally considered to be the fluctuation in bonds involving hydrogen atoms, often on the scale of 10 fs. To obtain sufficient time resolution for such a model, simulators often choose a time step on the order of 1-2 fs. To obtain 1 ns of simulation time, then, requires roughly $10^6$ updates of position/velocity/etc. for each of the particles in the system. Depending on the number and type of interactions modeled and the computational resources available, it is most likely possible to simulate from $10^6$ to $10^8$ time steps, restricting the total time scale to 100 ns or less. The fully atomistic resolution also places limitations on the length scales accessible, as the bond distances and ranges of motion are most often on the scale of angstroms, thus a typical all-atom
simulation deals with simulation systems hundreds to thousands of angstroms in diameter — a micron-sized simulation box is likely to be more than is necessary, as diffusion across the breadth of the simulation system is unlikely to take place on the time scale accessible, and the number of particles necessary to simulate such a large system will lead to a larger number of integrations of the equations of motion and a subsequent increase in the necessary computational time. Such large-scale simulations are not outside the realm of possibility, of course; the main factor regarding the feasibility of such simulations is the computational resources available for the task.

Normally, however, for systems consisting of larger molecules, simulation problems which take place over length scales than a few hundred angstroms or simulations taking place over time scales from 100 ns to several microseconds, fully atomistic resolution is either unnecessary or impractical. For systems in which the motion of individual hydrogen atoms is not as important as, for instance, the motion and interactions between large hydrocarbon chains or hydrocarbon segments of biological molecules, it is useful to implement instead a coarser model of the particles, such as united atom (UA) models which combine hydrogen atoms with the carbon or other atom types they belong to into a "superatom" representative of entire CHₙ groups[118–120]. Such models can maintain a high degree of chemical specificity based on the detailed form of the all-atom simulation but achieve increases in time and length scales by allowing for a longer time step (possibly 3-5 fs or more) and a reduction in the atomic degrees of freedom from the abstraction to the superatom groups.
Further abstractions are also available, in which groups of essentially
united-atom superatoms are combined into an even coarser model, such as in
MARTINI models[121, 122] designed for biomolecular simulations in which the
time scale of folding of protein/peptide or interactions at biological interfaces are
longer or system sizes are greater than can normally be handled by more detailed
simulation. In the latter form, a special reformulation of much of the methodology
of MD simulation was used and represents a fundamentally different paradigm, but
one that appears to have been successful in a number of trials.

In the extreme lie the fully generalized coarse-grained models such as the
bead-spring models found in the works of Kremer and Grest[123, 124], which
collect several heavy atom groups or entire chemical repeat units, in the case of
polymeric simulations. Abstraction to this level avoids fast motion associated with
not only hydrogen fluctuations, but also several levels of bond fluctuations from
much heavier atoms, allowing a much larger time step to be chosen and making
accessible simulation time scales that can range from microseconds to milliseconds,
although the nature of the coarse-grained Lennard-Jones time used in such a
generalized simulation makes a specific determination of the simulation potentially
difficult. In addition, the collection of atomic or even UA-like degrees of freedom
into such large superatoms effectively smooths the energy landscape results in
system dynamics that are substantially accelerated in comparison to all-atom or
united-atom simulations. The reduction in the number of degrees of freedom
versus a corresponding all-atom or united-atom representation further reduces the
system size necessary for large-scale simulations of polymeric systems, making it
possible to simulate far larger systems with similar computational overhead or
to reduce the computational overhead by reducing the computational size. Care must be taken in the interpretation of results from such a generalized model, however, as much of the chemical information that would have been present in all-atom or united-atom simulations is not present in a bead-spring model, so the data should be viewed in terms of general physical properties of polymers based on architectural effects and reduced representations of charge interactions. More specific interactions, reminiscent of hydrogen bonding, can be added through the inclusion of special effects in the bead-spring model[125], but the development of such potentials is nontrivial and outside the scope of the current investigation.

For any choice of simulation time scale, length scale and particle size/representation, the next and possibly most important choice in the simulation methodology is the choice of potentials for the interactions included in the system. In MD simulation, the collection of potential energy terms, their forms and associated parameters, is termed a force field. Force fields are of the most fundamental importance in MD simulations, as they govern the specific forces that act upon the particles in the simulation, and force fields are often designed to reproduce specific characteristics of the model systems either by matching the parameters in the functional forms of the force field in order to reproduce experimental data or by use of higher-level \textit{ab initio} quantum methods in order to base the derivation of parameters solidly from first principles.

Force fields can be developed specifically to optimize structure or dynamics for specific systems of interest (see recent work by Bhatta, et. al.[126, 127] in our own group for optimization of poly(3-hexylthiophene structure for MD simulations); such optimized force fields often focus on specific characteristics
of the model system, such as optimizing the packing of molecules in crystalline systems, and are highly connected to the range of state points for which they were developed. Even highly generalized force fields such as AMBER[128, 129], CHARMM[130, 131] and OPLS[120, 132], while highly similar in their functional forms and applicable to a wide number of possible systems for each, have been specially developed to be better suited to specific simulation systems (AMBER – biological systems, proteins and peptides; CHARMM – generalized, but also having optimized forms for proteins, nucleic acids and lipids; OPLS – specifically developed for liquid-state simulations, especially of organic liquids).

In the case of all-atom molecular dynamics simulations of methane and chloromethane adsorption on molybdenum (Chapter 3, the detail of all-atom simulation was deemed necessary based on the desire to investigate the specific choice of adsorption sites and energetics of adsorption as well as the adsorbate orientation and ordering near the substrate surfaces for small-molecule adsorbates on the time scale of individual small-molecule motion, which is sufficiently fast to not require more coarse-grained methods for extension to longer times. Longer time scales and length scales are specifically necessary in the case of large-scale macromolecular simulations such as those in Chapter 4, however, where the size and number of molecules becomes more than can be reasonably detailed using all-atom simulations and requires abstraction to the fully coarse-grained level. In the case of the bottle-brush polymers of interest in , reasonable sizes for experimentally accessible single bottle-brush polymers in work by Grubbs and colleagues[11], molecular weights from 100 kDa to 2,000 kDa and molecular sizes from 220 Å to more than 2100 Å, even all-atom or united-atom simulations of single bottle-brush molecules
approach the edge of accessible length scales, and the slow dynamics ostensibly associated with such large molecules suggest a necessity of a longer time step, both in order to avoid wasting resources in the simulation of dynamics too slow to capture and in the necessary extension of the overall simulation time scales to orders necessary to allow the systems to reach their equilibrium conformations.
CHAPTER III

ALL-ATOM MOLECULAR DYNAMICS SIMULATION OF MULTILAYER METHANE/CHLOROMETHANE ADSORPTION ON (100) SURFACE OF MOLYBDENUM (ADAPTED IN PART, WITH PERMISSION, FROM REF. [133]. ©2012 AMERICAN CHEMICAL SOCIETY.)

3.1 Adsorbate Construction and All-Atom Force Field and Parameters

The thin-film systems utilized in the simulations at the heart of this study were constructed initially through the equilibration of bulk liquid systems. Precursor systems of methane were originally prepared in two sizes — small systems of 1000 molecules and large systems of 2000 molecules — in order to study the effect of film thickness on surface behavior, while systems involving chloromethane were limited to 2000 molecules on the same substrate as a basis of comparison with the methane systems. System sizes were chosen in order to clearly represent a substantial thin-film adsorbate system while maintaining computational efficiency for the resources available.

In the equilibration procedure and the adsorption simulations, the model used to govern the interactions of the alkane adsorbates was the Optimized Potentials for Liquid Simulations – All-Atom (OPLS-AA) force field, originally developed by Jorgensen, et. al. [120, 132], in which the total potential energy of the system is given as the sum of separate potentials representing non-bonded, angle-bending, bond-stretching and dihedral torsion interactions (however, due to the
small-molecule adsorbate and non-bonded character of the substrates used here, the torsion interactions for the force field are neglected). In this force field, the non-bonded interactions are represented by a Lennard-Jones 12-6 potential with electrostatic interactions added via Coulomb potential:

\[
u(r_{ij}) = \begin{cases} 
4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] + \frac{e^2q_iq_j}{4\pi\epsilon_0\epsilon r_{ij}} & \text{if } r \leq r_c \\
0 & \text{if } r > r_c 
\end{cases}
\] (3.1)

Here, \(\sigma_{ij}\) and \(\epsilon_{ij}\) are the Lennard-Jones zero-potential distance and energy well depth, respectively, while \(r_c\) is the cutoff distance for the Lennard-Jones interaction — for these simulations, we have employed a 12 Å cutoff (15 Å has been suggested in the past as an appropriate cutoff for this type of simulation, but recent related simulations[134, 135] suggest that 12 Å is sufficient). The partial charges \(q_i\) and \(q_j\) are assigned to atoms \(i\) and \(j\); \(\epsilon_0\) is the vacuum permittivity and \(\epsilon\) is the dielectric constant (set to unity in the following). In keeping with the OPLS- AA model, geometric mixing rules were used for heteroatomic interactions. Values for \(\sigma\) and \(\epsilon\) for each adsorbate are given in Table 3.1.

Table 3.1: OPLS- AA non-bonded interaction parameters for methane and chloromethane (from [132])

<table>
<thead>
<tr>
<th>Atom type</th>
<th>(\epsilon_{ij}) (kal/mole)</th>
<th>(\sigma_{ij}) (Å)</th>
<th>(q(\epsilon))</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Methane</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.066</td>
<td>3.500</td>
<td>-0.24</td>
</tr>
<tr>
<td>H</td>
<td>0.030</td>
<td>2.500</td>
<td>0.060</td>
</tr>
<tr>
<td><strong>Chloromethane</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.066</td>
<td>3.500</td>
<td>-0.109</td>
</tr>
<tr>
<td>H</td>
<td>0.030</td>
<td>2.500</td>
<td>0.103</td>
</tr>
<tr>
<td>Cl</td>
<td>0.300</td>
<td>3.400</td>
<td>-0.200</td>
</tr>
</tbody>
</table>
Bond-stretching and angle-bending terms are both modeled as harmonic potentials:

\[
u_r(r_{ij}) = k_r \left(r_{ij} - r_{ij}^0\right)^2 \tag{3.2}
\]

\[
u_\theta(\theta_{ijk}) = k_\theta \left(\theta_{ijk} - \theta_{ijk}^0\right)^2 \tag{3.3}
\]

In this context, \(r_{ij}\) is the distance between directly bonded atoms \(i\) and \(j\), \(r_{ij}^0\) is the equilibrium bond length for the bond type represented by atoms \(i\) and \(j\), and \(k_r\) is an energy constant specific to the bond type represented by atoms \(i\) and \(j\). In this work, the values of the equilibrium bond length and energy constant are 1.090 Å and 331.0 kcal/mol for C-H bonds and 1.781 Å and 245.0 kcal/mol for C-Cl bonds, respectively. Similarly, \(\theta_{ijk}\) represents the bond angle created by consecutively bonded atoms \(i\), \(j\) and \(k\), and \(\theta_{ijk}^0\) is the equilibrium bond angle for the angle type represented by \(i\), \(j\) and \(k\). The energy constant \(k_\theta\) is also specific to the type of bond angle represented by the \(ijk\) triad. This study uses equilibrium angles of 109.5° and 107.6° for H-C-H and H-C-Cl bond angles, respectively, and bond-angle energy constants of 35.0 kcal/mol and 51.0 kcal/mol for H-C-H and H-C-Cl bond angles, respectively.

The end result of the equilibration process was a collection of bulk-liquid systems that we could then combine with prepared substrates in order to achieve the initial state for each of the production runs. After equilibration, the 2000-molecule methane adsorbate system produced an initial film of roughly twice the thickness of the 1000-molecule system when applied to the substrate, thus the 1000-molecule system came to be referred to as the ”thin” film and the 2000-
molecule system as the "thick" film. Chloromethane systems were produced in one system size, which produced a film of thickness comparable to the 2000-molecule methane film.

3.2 Substrate Construction and Force Fields

One of the primary concerns of this study is how differences in substrate structure or potentials representing substrate-substrate and substrate-adsorbate interactions affect the structure and dynamics of adsorbed molecules. To this end, two different surfaces were prepared for the adsorption simulations: a primary surface of crystalline molybdenum and a flat, featureless surface represented by a planar Lennard-Jones 9-3 potential (termed a "Lennard-Jones wall").

The Lennard-Jones 9-3 "wall" potential is derived from the same 12-6 potential used for the atomistic substrates. The idea behind its use is to represent an idealized surface — perfectly flat, structurally featureless, and possessing constant density identical to that of the atomistic surfaces — but with the same interaction characteristics as the atomistic substrate. The interaction potential is derived by integrating the 12-6 potential over the volume of space containing a "diffuse" half-lattice of particles comprising the substrate. As a result, the potential is a function only of the perpendicular distance from the surface, as components of the force parallel to the surface cancel one another due to the system symmetry. This creates a substrate that, subject to proper choice of coefficients, interacts with the adsorbate in the same fashion as an atomistic surface, but is more akin to a diffuse "slab" than an atomistic lattice. The potential derived from this integration is:
\[ u_{\text{wall}}(z) = \epsilon_{9-3} \left[ \frac{2}{15} \left( \frac{\sigma}{z} \right)^9 - \left( \frac{\sigma}{z} \right)^3 \right] \] (3.4)

Here, \( z \), the perpendicular distance above the surface, replaces the traditional \( r \) in the Lennard-Jones 12-6 potential. The potential length scale \( \sigma \) retains its interpretation from the original 12-6 potential, while the potential energy well depth \( (\epsilon_{9-3}) \) of the interaction now takes into account factors involving the reduced density \( (\rho \sigma^3) \) and integrated volume of the wall region. The end result is the Lennard-Jones 9-3 "wall" given above, possessing a modified value of the interaction well depth:

\[ \epsilon_{9-3} = \frac{2\pi}{3} \rho \sigma^3 \epsilon_{12-6} \] (3.5)

In order to create a Lennard-Jones substrate as a direct analog to the crystalline molybdenum, the parameters of the wall potential were chosen to match the Lennard-Jones 12-6 parameters for an all-atom molybdenum substrate, reported below.

The primary substrate for the set of simulations in this study was solid molybdenum, a crystal possessing a BCC structure (lattice parameter \( a = 3.147 \text{ Å} \) [136]). The molybdenum crystal was composed of 3072 atoms in a slab with a square surface 50.35 Å in each direction along the surface and 18.88 Å in thickness. In the framework of this study, in which one of the central facets under investigation is the effect of the type of interatomic potential used to govern the molybdenum substrate, two specific interatomic potentials were employed. The first of these used was a simple Lennard-Jones 12-6 potential, which integrates...
easily with the OPLS force-field used for the liquid adsorbates. In such a formulation, however, the Lennard-Jones parameters regarding the molybdenum substrate must be taken from an appropriate model for metallic systems. In the simulations that follow, the characteristic energy well depth of the Lennard-Jones interaction ($\epsilon$) was set at 23.36 kcal/mol, and the characteristic length scale ($\sigma$) was set at 2.74 Å, values reported from the literature [137]. As previously mentioned, the values of the interaction parameters for the Lennard-Jones 12-6 interaction dictate $\epsilon_{9-3}$ for the Lennard-Jones substrate, thus giving $\epsilon_{9-3}$ a value of 64.584 kcal/mol.

However, even if the Lennard-Jones parameters for the molybdenum can be adapted from an appropriate model, shortcomings in using pairwise potentials to model metallic systems may limit the accuracy of the substrate structure obtained. The possibility of inaccuracy in modeling metallic solids and their interactions with liquids when utilizing pairwise potentials was one of the factors anticipated when choosing the second interatomic potential used in this study.

The embedded-atom method (EAM) of Daw and Baskes [138] seeks to more accurately represent metallic systems by establishing a total potential for a group of atoms based on the electron density of the system, treating each atom as an impurity within a host environment of the other atoms and deriving an *embedding energy*, $F$, for the energy required to place the embedded atom at a certain position. A correction is also added to take into account core-core repulsion which takes the form of a pairwise potential between individual pairs of atoms. The basic form of the EAM potential (and the definition used in the simulations) is then
\[ E_i = F_i \left( \sum_{j \neq i} \rho_i(r_{ij}) \right) + \frac{1}{2} \sum_{j \neq i} \phi_{ij}(R_{ij}) \quad (3.6) \]

Here, \( F \) represents the embedding energy, dependent on the electron density \( \rho \), at the location of atom \( i \), and \( \phi \) represents the pairwise interaction potential between atom \( i \) and an atom \( j \) at a distance \( R_{ij} \). For the molybdenum substrate used in these simulations, the general forms of \( F \) and \( \phi \), as well as some parameters for molybdenum, have been taken from the literature[139].

It should be noted that the very different forms for the pairwise Lennard-Jones potential used for the adsorbate liquids and the many-body EAM potential used for some of the molybdenum substrates leaves a question of how to describe the interaction between the two. In such cases, a Lennard-Jones 12-6 potential was used for these interactions, using parameters for molybdenum taken from the parameters used for the Lennard-Jones substrate model. Thus, the heart of the investigation lies in how the adsorbate-substrate and substrate-substrate interactions compete to change the surface structure of the substrate and influence liquid adsorption at the interface.

This requires a surface that has some level of mobility associated with it, or at least one that has the freedom to move. While the molybdenum substrate as constructed here is intended to model a metallic crystalline structure, little difference between substrate potentials would be expected if the substrate atoms were always completely immobilized in their crystalline positions. On the other hand, if even slight perturbations from the ideal crystal positions were allowed, it is possible that subtle variations would begin to appear in the potential energy, which would then propagate through not only the substrate, but the adsorbate
as well, as a result of changes to the substrate-adsorbate interactions. Thus, we further divided systems involving the Lennard-Jones substrate into ”mobile” systems, in which substrate atoms within 10 Å of the surface were given freedom to move (with the remainder, out of range of surface substrate-adsorbate interactions, kept at fixed positions), and ”frozen” systems, in which the substrate atoms were fixed in their crystalline positions. Simulations involving the EAM substrate, by this token, are all classified as ”mobile”. The permutations of substrate potential, system size and surface-atom mobility on which this study focuses are presented in Table 3.2.

Table 3.2: Definitions of simulation system shorthand

<table>
<thead>
<tr>
<th>Substrate Potential</th>
<th>Mobility</th>
<th>System Size</th>
<th>In-text reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Methane</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lennard-Jones 9-3</td>
<td>N/A</td>
<td>2000 molecules</td>
<td>L-J wall</td>
</tr>
<tr>
<td>Lennard-Jones 12-6</td>
<td>Frozen</td>
<td>1000 molecules</td>
<td>thin L-J frozen</td>
</tr>
<tr>
<td>Lennard-Jones 12-6</td>
<td>Frozen</td>
<td>2000 molecules</td>
<td>thick L-J frozen</td>
</tr>
<tr>
<td>Lennard-Jones 12-6</td>
<td>Mobile</td>
<td>2000 molecules</td>
<td>thick L-J mobile</td>
</tr>
<tr>
<td>EAM</td>
<td>Mobile</td>
<td>2000 molecules</td>
<td>EAM</td>
</tr>
<tr>
<td><strong>Chloromethane</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lennard-Jones 9-3</td>
<td>N/A</td>
<td>2000 molecules</td>
<td>L-J wall</td>
</tr>
<tr>
<td>Lennard-Jones 12-6</td>
<td>Frozen</td>
<td>2000 molecules</td>
<td>L-J frozen</td>
</tr>
<tr>
<td>Lennard-Jones 12-6</td>
<td>Mobile</td>
<td>2000 molecules</td>
<td>L-J mobile</td>
</tr>
<tr>
<td>EAM</td>
<td>Mobile</td>
<td>2000 molecules</td>
<td>EAM</td>
</tr>
</tbody>
</table>

All simulations, whether bulk liquid equilibration, liquid/molybdenum equilibration or liquid/molybdenum production runs, were performed using the LAMMPS molecular dynamics simulation package[140], with a time step of 1 fs. Integration of the equations of motion was performed using the velocity-Verlet algorithm.
Figure 3.1: Initial configuration of equilibrated films of thick-film methane and chloromethane, both on molybdenum (green spheres). The adsorbate portions of each case were taken from equilibration runs and represent the final density from that process; during production runs, the film thicknesses adjusted to reported values.

The adsorbate portions of each simulation system were taken from the final state of a separate bulk equilibration simulation performed in the isothermal-isobaric (NPT) ensemble with periodic boundary conditions extended in all directions. The purpose here was to allow the adsorbates to reach equilibrium at the proper bulk liquid density before being applied to the substrate. In all cases, equilibration was performed at fixed temperatures above the respective bulk melting temperature of each compound (CH\(_4\): 90.66 K[141], CH\(_3\)Cl: 175.55[142]), utilizing a Nosé-Hoover thermostat with a 100 fs damping time in order to maintain a nearly constant temperature. An external pressure of 1 atm was maintained by use of a Nosé-Hoover barostat, with a 1 ps damping time applied.

The equilibrated liquid molecules were then transferred to a substrate system, leaving 5 Å of vacuum between the substrate surface and the lowermost edge of the adsorbate. This was done to avoid presenting some molecules in
positions where they could be considered already adsorbed and thus to allow the largest possible leeway in choice of adsorption sites for adsorbate molecules within range of the surface. Snapshots of the initial system configurations are presented in Figure 3.1. Adsorption simulations were performed in the canonical (NVT) ensemble, with temperature controlled by Nosé-Hoover thermostat in the same way as for liquid equilibration. These simulations were found to equilibrate within 3 ns ($3 \times 10^6$ time steps), after which production runs were performed for 0.5 ns to collect data for analysis. Atom positions for the equilibration procedure were reported every 5-25 ps for monitoring of vital system parameters, while atomic position data was collected every 1 ps during the production runs for detailed analysis.

Production runs for adsorption-centric systems were aimed at exploring behavior over the entire range of temperatures at which the adsorbate is expected to remain liquid (or nearly so); in the case of methane, this means runs were performed at 90 K, 95 K, 105 K and 110 K, ranging from just below the bulk melting temperature to just above the bulk boiling point (109.15 K[143]), while for chloromethane, runs were performed at 185 K, 205 K, 225 K and 245 K, from above the bulk melting temperature to just below the bulk boiling point at 249 K[144]. In adsorption simulations, periodic boundary conditions were extended in the x and y directions (along the plane of the surface), but not in the z-direction, effectively creating the film-substrate system; the method used to calculate long-range electrostatic interactions was subsequently modified to take into account this lack of periodicity in the z-direction.
While the Lennard-Jones interactions were truncated at the 12 Å cutoff previously established, to assume the Coulomb potential is similarly negligible is unwise, although calculating this long-range interaction generally occupies a significant fraction of the simulation time. To reduce the computational overhead associated with the Coulomb force calculation, the particle-particle/particle-mesh Ewald summation method[145] was used, with a boundary imposed between real-space and momentum-space calculations; the cutoff used here was also 12 Å.

3.3 Structure of Methane Films

In Figure 3.2, the average mass density profiles of adsorbed methane films are presented as a function of the distance normal to the substrate surface, with the zero point of the density taken as the position of the wall in cases involving a wall substrate or the position of the plane containing the centers of the uppermost molybdenum layer in cases involving an explicit molybdenum substrate. The density profiles have been calculated by partitioning the adsorbate region into bins of width $\delta z$ (fixed at 1 Å) along the surface normal direction (z-axis), summing over the atomic masses of all atoms present within a given bin and normalizing by the volume of each bin, which is constant due to the fixed surface area and the choice of $\delta z$.

As with previous related adsorption studies[134, 135], we note ordered layering in the film by the presence of oscillations in the average mass density profile. In the case of thin-film adsorption on the Lennard-Jones molybdenum substrate, as well as the case of adsorption on the Lennard-Jones 9-3 wall at 90 K, pronounced oscillations persist throughout the film to the film-vapor interface.
(Figure 3.2, a-b). In the thin-film case, however, we note that the thin film itself appears to be severely limited in depth, existing to 17–18 Å, or less, given evaporation at 110 K. In cases involving larger adsorbate systems, identifiable oscillations persist even at higher temperatures in the simulation range to depths of 20-25 Å, suggesting that layering persists throughout the thin-film systems because the majority of the system is always within the range of interaction with the substrate.

In the case of adsorption on the Lennard-Jones wall (Figure 3.2a), the size of density oscillations and lack of decay in oscillation amplitude suggest that while ordered layering persists to the film-vapor interface at the lowest studied temperature (90 K), significant reordering of layers near the interface takes place even after a modest increase to 95 K. It is possible that this reordering presents itself due to a traversal of the bulk melting temperature of methane between simulations at 90 K and 95 K (the bulk melting point[141] lies at 90.66 K). At 90 K, it is quite possible that the majority of methane molecules remain in a rigid solid-like phase, while at 95 K, the density suggests a more liquid-like region near the film-vapor interface and reveals the extent of substrate-adsorbate interactions near the solid-liquid interface.

In general, as the temperature increases, density oscillations near the vapor interface begin to decay in amplitude, approaching a nearly constant value close to that of the bulk liquid density (0.427 g/cm³ at 108 K[146]). In Figure 3.2, on the Lennard-Jones wall, the average density in the bulk-like region is approximately 0.46 g/cm³, suggesting a slight density enhancement and perhaps closer packing near the substrate surface, while on the molybdenum substrates, the av-
Average density in the bulk region is closer to 0.43 g/cm$^3$, very close to the bulk value. Adsorption on the EAM molybdenum surface, however, seems to exhibit a greater degree of enhancement than even methane on the LJ wall (approximately 0.54 g/cm$^3$), which may be caused by the presence of small-amplitude oscillations nearly to the vacuum interface itself. In all cases, we observe that layering appears to persist to four to five distinct layers, with the amplitude of oscillation weakly dependent on temperature for adsorption on the non-wall substrates.

Comparing the first-layer peak density across substrates, we see that the amplitude is quite nearly identical in each case, even as the temperature rises 20 K over the course of the simulations; only for the Lennard-Jones wall substrate does the density of the second adsorbed layer decrease significantly over the temperature range studied. Beginning with the third adsorbed layer and beyond, temperature effects once again begin to show a decrease in peak density along with increasing temperature, culminating in the temperature-dependent decrease.
in the bulk density near the vapor interface. The enhancement of the mass density in the oscillatory regions near the substrate-adsorbate interface is indicative of the ordering of layers at or near the surface, with the amplitudes themselves indicative of the relative order imposed.

The density fluctuations for the first adsorbed layers on each substrate show comparable width (roughly 3 Å) and shape but subtly differing amplitudes, suggestive of the differences in the ordering imposed from interaction with the substrate. The mobile Lennard-Jones substrate (Figure 3.2d) shows the lowest peak density in the first layer, as well as slightly lower peak densities in the second and third adsorbed layers, which suggests at first glance that increased atomic mobility in the substrate surface may lessen the extent of ordering imposed on adsorbed layers near it. On the other hand, the density profile of methane adsorbed on the EAM molybdenum substrate exhibits some of the highest peak densities in the first three layers of all substrates studied. Higher densities for the layers nearest the EAM substrate suggest possible differences in the ordering imposed on these first adsorbed layers.

What the width of the first-layer regions suggests is that, for each substrate, the supported first layer is essentially no wider than a single adsorbate molecule, and that the deviation in mean position of the molecules within this single-molecule layer is fairly small. Thus, the first layer, at the very least, appears to be dominated by the two-dimensional packing arrangement admitted by interaction with the surface as well as neighboring molecules. If this surface layer can be treated in essence as a two-dimensional collection of molecules, it may be quite useful to probe the two-dimensional positional order by examining the
pair correlation function, $g(r)$ (also known as the radial distribution function, or RDF). We calculate $g(r)$ in these cases similarly to previous work\cite{134, 135} and as has been presented in other work\cite{147}. Given the position of a reference particle, we can create a histogram of the number of other molecules within a shell $dr$ of the reference particle at a distance $r$; normalization with respect to an uncorrelated system then provides the measure of $g(r)$. The radial distribution function gives the probability of finding another particle at a distance $r$ from the reference position and provides significant information about spatial arrangement. It can be used to determine the average number of nearest neighbors of molecules within the simulation, as well as the nearest-neighbor distances, and is of additional importance to computer simulations as it can be linked to the static structure factor, $S(q)$, from X-ray or neutron diffraction\cite{148, 149} or low-energy electron diffraction\cite{150} and thus provides a connection between experiment and simulation.

In all cases, whether focused on methane or chloromethane, the radial distribution function presented employs the position of the central carbon atom in as a marker for the position of the molecule. In the case of methane, this assumption is justified — the position of the central carbon marks both the center of mass of the molecule as well as its geometric center. For chloromethane, the asymmetry introduced by the inclusion of the larger halogen atom moves the center of mass away from the molecule’s geometric center and the carbon position; however, using the carbon position as the position of the molecule remains a useful tool. Therefore, references in this and successive sections to $g(r)$ should be
understood to reflect specifically the carbon-carbon radial distribution function, $g_{C-C}(r)$.

![Figure 3.3: Plot of radial distribution function, $g(r)$, for CH$_4$ for the eight layers closest to the L-J wall at 90 K. Vertical dashed lines represent positions of peaks expected for perfect hexagonal packing based on nearest-neighbor distance seen in first layer.](image)

In Figure 3.3, the radial distribution function has been calculated and plotted as a function of the radial distance for each discernible layer of methane formed on the Lennard-Jones wall at 90 K; this case produced the greatest number of distinct layers (8), and can be used to examine clearly the relationship between lateral order within the layers and the distance of the layer from the substrate surface.

Previous studies investigating neutron diffraction[151, 152] and heat capacity[153] to elucidate the surface-layer structure of methane on graphite have shown that near monolayer coverage, adsorbed layers can arrange in a commensurate solid phase, depending on temperature. The structure generally observed or inferred in this phase involves imposed two-dimensional hexagonal order, with
molecules arranged into an array of $\sqrt{3} \times \sqrt{3}$ cells at monolayer completion. While graphite does possess some surface structure as opposed to the perfectly flat Lennard-Jones wall, it is generally considered sufficiently flat that the structures seen on graphite suggest a good comparison for methane adsorbed at the wall surface. Thus, in Figure 3.3, we also choose to note with vertical dashed lines the positions of $g(r)$ peaks that would be suggested by a perfect hexagonal structure, given the same nearest-neighbor distance predicted. The calculated nearest-neighbor distance between carbon atoms for methane on the Lennard-Jones wall was 4.1 Å, just slightly less than carbon-carbon nearest-neighbor distance (4.26 Å) for the $\sqrt{3} \times \sqrt{3}$ structure on graphite, indicating layers on the Lennard-Jones wall are slightly compressed, compared to monolayer methane on graphite, but the agreement between the calculated peaks for a perfect hexagonal layer and the observed $g(r)$ peaks suggest the comparison is a good one. We can verify the orderly arrangement of methane molecules visually in Figure 3.4, where we have visualized only the first adsorbed layer of methane molecules on the Lennard-Jones wall, with the wall not included in the figure.

Figure 3.4: Top view of first adsorbed layer of methane molecules (carbon in blue, hydrogen in white) on the Lennard-Jones wall at 90 K (wall not visible).
It becomes readily apparent, then, that at low temperatures, methane molecules in the first adsorbed layer on the Lennard-Jones wall take positions very close to those expected for a hexagonally-packed surface-adsorbed layer, as evidenced by the amplitudes and positions of the major peaks seen. Indeed, the first four adsorbed layers at 90 K show peak placement that mirrors the expected placement of hexagonally-packed layers up to 17-18 Å, which would appear to indicate intermediate- to long-range order and adherence to the hexagonal packing arrangement expected of methane. As one moves further from the substrate, however, the split peaks that indicate regular hexagonal packing begin to merge and decrease in peak amplitude, suggesting variations in the numbers of first-nearest neighbors as well as wider variability in the packing arrangement; hexagonal order clearly is a decreasing function of proximity to the surface, as one might expect.

One feature of the first peak in Figure 3.3 is a slight leftward shift in first-nearest-neighbor position moving further from the surface. This change appears to represent at most a change of tenths of an angstrom yet represents what might be a slight compression of the local structure. It may be possible to explain this shift by noting that as the first-nearest-neighbor peak shifts to slightly lower \( r \), the amplitude of this peak decreases, and \( g(r) \) in the trough region just beyond the first peak increases. Combined, they suggest that variability in the nearest-neighbor positions may be resulting in defects which preclude the orderly hexagonal arrangement seen in the first few layers, and may suggest five or fewer neighbors for many particles in the first layer; fewer neighbors would allow each of them to pack slightly closer together, thus shifting the first peak to lower \( r \).
Figure 3.5: Plot of $g(r)$ for the first four layers of CH$_4$ on the L-J wall at 95 K (left), 105 K (center), and 110 K (right).

Moving to even slightly higher temperatures, as evidenced in Figure 3.5, produces a significant change in the positional order seen. There is no longer the clear pattern indicative of hexagonal packing; indeed, it is not clear that there is significant solid-like ordering at all, although the presence of oscillations in $g(r)$ to 25 Å suggests some sort of long-range positional order is available, at least for the three layers closest to the substrate surface. In the fourth layer, the rapid decay to unity suggests little, if any, positional order at this depth, and while the third layer shows some manner of oscillation not present in the fourth, it is clearly diminished compared to the first two layers, which show very similar profiles. At the same time, the leftward shift seen in the first-nearest-neighbor peak in the case of adsorption at 90 K is now more pronounced in all examples in Figure 3.5, suggesting that at elevated temperatures, as one moves further from the substrate surface, increased mobility may cause increased numbers of defects or particles even moving out of the layers near the surface and toward the vacuum, allowing for closer packing near the surface.
Thus, the presence of two-dimensional hexagonal packing in adsorbed layers of methane on a Lennard-Jones wall at 90 K can be established, but the next question is whether this type of order carries over to the molybdenum substrates or is modified by the presence of the atomic substrate. To that end, $g(r)$ has been plotted in Figure 3.6 for methane adsorption on each of systems with a explicit molybdenum structure.

![Figure 3.6: Plot of $g(r)$ for the first three layers for thin-film L-J frozen (a), thick-film L-J frozen (b), thick-film L-J mobile (c), and EAM (d) systems of methane adsorbed on molybdenum at 90 K](image)

Immediately observed is the presence of some form of structure for the first adsorbed layer on each of these substrates, while the second and third layers show slight ordering and little clear structure. In the first layer, the presence of many small peaks of limited width suggest a form of solid-like structure at this temperature, but it is clear that this order does not resemble the hexagonal structure seen on the L-J wall. However, to a distance of 10 Å or more, the different patterns overlap to a great extent, suggesting that although it isn’t clear what type of order is at work here, it could be related quite simply to the presence of
the molybdenum surface structure. The radial distribution function suggests no solid-like packing arrangement at temperatures above 90 K, although the smooth oscillations seen may suggest some very weak positional order at these temperatures.

Beyond the first layer, the radial distribution function in each case shows no clear solid-like packing arrangement at 90 K and suggests that whatever structure is induced at the surface by the surface of the molybdenum substrate penetrates very weakly into the bulk of the adsorbate; though some oscillations are seen and the amplitudes do not decay to unity immediately, the lack of specific features in the radial distribution function suggests a large amount of variability in the packing arrangements of methane in the second layer and beyond.

3.4 Structure of Chloromethane Films

![Density plots](image)

Figure 3.7: Average mass density as a function of distance from the substrate surface for chloromethane adsorbed at 185 K on the (clockwise from upper left) EAM substrate, frozen L-J, mobile L-J and L-J wall.

Owing to the replacement of a hydrogen by a much more massive chlorine atom (without a commensurate increase in atomic volume), the density of
chloromethane will be substantially larger than that of methane. The bulk density obtained from our simulations, taken from the value of the density in the plateau region of the densities shown in Figure 3.7, confirms this assumption, suggesting the bulk density of chloromethane is 1.03 g/cm³ at 205 K for chloromethane on the molybdenum substrates and 1.06 g/cm³ on the Lennard-Jones wall, (for reference, the calculated value from a modified Rackett equation[154] is 1.07 g/cm³ at 205 K). There is a significant enhancement of the average mass density in the region of the first adsorbed layer, much larger than that seen for methane on any of the substrates. Not only is the enhancement of the mass density much more pronounced in the first adsorbed layer, but the peak itself appears to be significantly narrower than the analogous peaks for methane on any of the substrates. As the majority of the mass of a chloromethane molecule is concentrated in the chlorine (and carbon, to a lesser extent) atoms, this suggests that the narrow, highly enhanced mass density peak corresponds to a concentration of chlorine atoms, as well as carbon, within a narrow band in the z-direction, which in itself suggests a preferred orientation for the chloromethane molecules, inasmuch as it would suggest that the C-Cl bond is either directed parallel to the surface or is deflected only slightly. This result is supported by previous work[135] in which we determined that when bromine or chlorine were substituted for a fluorine atom on a CF₄ molecule, and the resulting system was allowed to adsorb on graphite, CF₃Br and CF₃Cl populations at the surface tended to prefer orientations that placed the C-Br or C-Cl bond at an angle just beyond 90 degrees to the surface normal, or just below a plane parallel to the surface. The substitution of chlorine
for hydrogen in this case presents, we believe, a similar symmetry-breaking and thus leads us to believe CH$_3$Cl should show a similar orientation.

For comparison, experimental data for adsorption of CH$_3$Cl on graphite shows some difference, however, in molecular orientation dependent on the coverage of the surface layer. X-ray diffraction of CH$_3$Cl on graphite[155] suggests two structures for the first adsorbed layer, both based on a 2D rectangular cell. At high coverage, the rectangular cell permits two molecules per cell, each with C-Cl axis canted at roughly 18° to the surface normal; the orientation of the C-Cl bond vectors alternates between "up" (Cl away from the surface) and "down" (Cl toward the surface) between similarly aligned rows. This result was previously noted in MD simulation of CH$_3$Cl adsorbed on Xe-coated graphite[156]. At lower coverage, the C-Cl bond vectors are oriented nearly parallel to the surface, similar to the findings in this study and to single-molecule MD simulation[157], although within the plane, the molecules appear to prefer a "zig-zag" ferroelectric order that could not be identified in the present study. A more thorough analysis of the adsorption on graphite of CH$_3$Cl and numerous related molecules may be found in the review work by Knorr[158].

More support for this result may be available from visualizing the simulation system to qualitatively discuss the arrangement of C-Cl bond vectors. Using VMD[159], we can prepare a simple snapshot of the first layer of our CH$_3$Cl simulation system adsorbed on the L-J wall, which is presented in Figure 3.8.

A top view of the first adsorbed layer of CH$_3$Cl on the Lennard-Jones wall shows that the majority of chlorine atoms neither occlude nor are occluded by carbon or other hydrogen atoms in the molecule, and it would appear in the
majority of cases that the C-Cl bond vector extends far enough to suggest the angle of inclination either away from or toward the surface is relatively small.

The orientation of the C-Cl bond vectors within the plane of the first adsorbed layer, however, does not appear to hold any measure of discernible long-range order as the methane on the L-J wall did. In Figure 3.9, we have plotted the carbon-carbon radial distribution function for CH$_3$Cl systems on each of our substrates in order to examine any possible spatial correlations.

![Figure 3.8: Top view of the first adsorbed layer of CH$_3$Cl molecules (blue – C, white – H, yellow – Cl) on the Lennard-Jones wall (not visible) at 185 K.](image)

![Figure 3.9: Radial distribution function as a function of the interparticle spacing, $r$ for CH$_3$Cl molecules on each of the substrates at 185 K: (clockwise from upper left) EAM, Frozen L-J, Mobile L-J and L-J 9-3 wall.](image)
The radial distribution functions in Figure 3.9 immediately suggest that there is no clear global information to be gleaned regarding two-dimensional spatial correlations in these systems with the data at hand; it is not even the case for all substrates that temperature does not appear to affect the positioning of the \( \text{CH}_3\text{Cl} \) molecules on the surface. To this end, adsorption on the Lennard-Jones wall shows the least variability with respect to temperature, but also shows little beyond short- to intermediate-range order of any sort. With the exception of the L-J wall, the plots of RDF in Figure 3.9 show broadly similar peak structure and amplitude, both with respect to one another and to different temperatures on the same substrate, but there is no discernible packing arrangement in the specific form of the RDF, suggesting that the most that can be said about surface positional correlation in this case is that there is some short to intermediate order for adsorption on the L-J wall, along with a more nebulous intermediate- to long-range structure on the non-wall substrates.

3.5 Binding Energy: Correlation with Surface Sites

The previous sections have attempted to give an explanation for the observed surface structures based on structural considerations (average mass density, radial distribution function). Another main effort of this study has been to investigate how the interaction between the adsorbate and surface, and specifically between adsorbate molecules and specific surface adsorption sites, would affect the overall structure of the adsorbed layers. To do so, we propose to look at correlations between the surface structure, available surface adsorption sites and the adsorption preferences thereof to determine what types of adsorption sites are
most probable and therefore likely most advantageous for adsorption of the given species. To do this, we have performed a very basic calculation of the binding energy for molecules at the interface as a function of the type of adsorption site the adsorbate molecules occupy.

The first step in determining the preferred adsorption sites is to identify different possible adsorption sites for each substrate. The Lennard-Jones wall, being featureless, has only one type of "binding site" — a molecule is either adsorbed or it is not. Subtle differences in binding energy based on the orientation of the adsorbing molecule are expected to exist but are outside the scope of the current investigation and are expected to be of limited magnitude. In the case of adsorption on molybdenum, however, we have identified three basic types of surface adsorption sites based on the substrate’s body-centered cubic structure:

The calculation of binding energy is a rough estimate: several candidate molecules conforming to the criteria of the adsorption sites were chosen from systems of each adsorbate-substrate combination, and for each, the following quantity was calculated:
\[ E_{\text{binding}} = E_{\text{mol+sub}} - (E_{\text{mol}} + E_{\text{sub}}) \] (3.7)

Here, \( E_{\text{mol+sub}} \) refers to the potential energy (separated from the kinetic energy, thus independent of temperature) of a system composed of substrate and the chosen representative adsorbed molecule with all other adsorbate molecules removed, whereas \( E_{\text{mol}} \) refers to the potential energy of the representative molecule alone, with the substrate removed, and \( E_{\text{sub}} \) refers to the potential energy of the substrate without any adsorbate molecules whatsoever. As such, a preferred adsorption site will have a lower bound-state potential energy than the combined potential energy of its components and the binding energy reported should be negative, and after the calculations, this was indeed the case. Thus, only the magnitude of the binding energy is reported in Table 3.3.

Though the "atop" site was identified as a possible adsorption site on the molybdenum surface, during the course of the calculation of the average binding energy it was discovered that the population of molecules adsorbed on an "atop" site was effectively zero, as no such adsorbed molecules were observed in the systems used to perform the calculations. Thus, in the current investigation, there are only two feasible adsorption sites: "interstitial" sites and "bridge" sites.

In both cases, the Lennard-Jones "wall site" has the lowest binding energy of all calculated binding sites; the difference in potential energy between adsorbing on the Lennard-Jones wall and not doing so is, relative to other binding energies, fairly substantial. Thus, it seems reasonable to assume that given no alternatives, it is preferable for molecules to maximize adsorption on the wall, even if it is
Table 3.3: Binding energy estimates for chosen sites on the molybdenum surface for methane (top) and chloromethane (bottom) molecules adsorbed at the given sites. Energies are given in kcal/mol, and values given are the magnitude of the reduction in energy as a result of binding; i.e., higher values represent more favorable binding.

### Methane:

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Sites</th>
<th>Atop</th>
<th>Bridge</th>
<th>Interstitial</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wall</td>
<td>11.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>EAM</td>
<td>–</td>
<td>12.4</td>
<td>15.6</td>
</tr>
<tr>
<td></td>
<td>Mobile LJ</td>
<td>–</td>
<td>16.8</td>
<td>17.7</td>
</tr>
<tr>
<td></td>
<td>Frozen LJ</td>
<td>–</td>
<td>17.7</td>
<td>20.5</td>
</tr>
</tbody>
</table>

### Chloromethane:

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Sites</th>
<th>Atop</th>
<th>Bridge</th>
<th>Interstitial</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wall</td>
<td>20.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>EAM</td>
<td>–</td>
<td>31.6</td>
<td>25.4</td>
</tr>
<tr>
<td></td>
<td>Mobile LJ</td>
<td>–</td>
<td>26.9</td>
<td>26.3</td>
</tr>
<tr>
<td></td>
<td>Frozen LJ</td>
<td>–</td>
<td>31.7</td>
<td>29.6</td>
</tr>
</tbody>
</table>

possible that they would prefer not to bind to such a featureless construct, were there an alternative to which to bind.

In the case of methane, aside from the low binding energy of the Lennard-Jones wall relative to the molybdenum substrates, it is discovered that the interstitial sites are categorically preferred, and in the case of the EAM and frozen L-J substrates, noticeably so. We suggest that this may be related to the shape of the methane molecule — the symmetry of the hydrogens presents an overall molecule that is spherical or nearly so, and thus is least obstructed when attempting to access the interstitial sites. The interstitial sites then tend to maximize the number of contacts between the adsorbate and the substrate, presenting a significant advantage. However, while in two of the cases the difference in binding
energy between the interstitial and bridge sites is significant, it is not overwhelming enough to suggest a very strong preference for the interstitial sites. This may be due to overall adsorbate molecule size, and whether the adsorbate can effectively minimize the distance to the substrate atoms to make the interstitial sites overwhelmingly advantageous.

In the case of chloromethane, on the other hand, while the Lennard-Jones wall binding site presents a significantly lower binding energy than any molybdenum substrate (more than 20% less than the next lowest), the preference of the bridge sites vs. interstitial sites is reversed. While it is true again that the mobile L-J molybdenum substrate presents the smallest differential between interstitial-site and bridge-site binding energy, it is true that in all cases, the bridge sites are at least slightly preferred to the interstitial sites, and in the case of the EAM substrate, the bridge sites are substantially preferred. We suggest that this difference is likely due again to the shape of the adsorbate molecule, which has a significant asymmetry caused by the inclusion of chlorine and thus creates a molecule likely in the shape of a prolate spheroid. The shape factor may be either the cause of or may be affected by the propensity of chloromethane molecules to orient their dipoles nearly parallel to the substrate surface, and this may in turn be either the cause or a contributing factor to the choice of adsorption site. Because of the larger molecule size and distorted shape, it is probable that the chloromethane molecule has difficulty orienting within the interstitial sites, either due to hindrance from neighbor adsorbate molecules or due to interactions with the substrate, and thus it may be that the preferred orientation prefers to attempt to separate the chlorine and carbon sites of the molecule across the bridge site in an attempt to bring
both as close to maximizing contacts with the substrate, rather than reorient the molecule in order to maximize surface contacts with only the carbon or chlorine.

Clear comparison with other simulated systems or experimental results may prove difficult in cases such as these; we are aware of few reliable estimates of binding energy for the physisorption of methane on molybdenum metal and even fewer regarding adsorption of chloromethane. In a simulation study of methane adsorption on molybdenum oxides, estimates of binding energies fell in the range of roughly 2-13 kcal/mol, depending on the oxygen content of the oxide[70], and DFT simulations of adsorption of methane on graphite and carbon nanotubes[160] suggest an adsorption energy of roughly 3.5 kcal/mol on graphite. Similarly, simulations of methane adsorption on the (111) face of palladium metal[161] suggested an adsorption energy of 16.5 kJ/mol (3.9 kcal/mol), significantly below the calculated binding energies presented here. The difference is likely largely accountable to the large energy-well depth associated with the Lennard-Jones interaction for the molybdenum substrate; assuming this value is itself not in error, the differences suggest the molybdenum surface interacts noticeably more energetically with adsorbing species than the noble metals often seen.

Qualitatively, we may examine visualizations of the simulation systems in order to obtain some measure of confidence regarding our reasoning for the binding-site preferences seen above. Two such visualizations, presenting methane and chloromethane adsorbed on an EAM substrate, are presented in Figure 3.11.

In the visualizations lies a small measure of confirmation of the prescribed binding behavior: in Figure 3.11(a), it seems clear that a significant number of methane molecules prefer to reside in the region in the center of a unit-cell face,
while in Figure 3.11(b), one can see a number of chloromethane molecules stretching their C-Cl bonds across the region between adjacent molybdenum atoms, as well as indication of the disordered arrangement of dipoles within the first adsorbed layer that made the radial distribution function difficult to analyze.

Aside from the implications of binding-site preference, the estimates of binding energy may also give us information regarding the differences between the different approaches to the treatment of the substrate. For both adsorbate molecules, for instance, the EAM potential for the substrate resulted in the largest differential between the bridge- and interstitial-site binding energies, slightly larger than the frozen Lennard-Jones substrate and considerably larger than the mobile Lennard-Jones substrate, although in neither case were the binding energies on the EAM substrate greater than the Lennard-Jones substrates. This may be a difficult result to analyze; the similarity in the energy differential between the EAM and the frozen L-J substrate might suggest that the EAM provides a more rigid potential
for the molybdenum in that at the same time the model allows mobility in surface atoms, the potential prevents substantial mobility and favors the energetically probable binding interaction. At the same time, while the difference in binding energy between sites for the EAM and frozen L-J substrates were comparable, in all but bridge-site adsorption of chloromethane, the actual estimate of binding energy for the frozen L-J substrate was 20–30% larger than the EAM values, and even the binding energies for the mobile Lennard-Jones substrate were noticeably higher. This could suggest that the EAM potential is actually more flexible toward surface structure. Additional parameters are likely to play key roles in the overall picture, however: adsorbate size may affect accessibility of surface sites, total substrate mobility may confirm whether the EAM is fundamentally more flexible or more rigid, etc. These questions are currently best left to future endeavors and may provide an interesting glimpse into fundamental adsorption behavior.

3.6 Conclusion

We have herein examined the structure, packing and orientation of methane and chloromethane molecules on the (100) surface of molybdenum metal, as well as estimated the energy of adsorption for these species, by using all-atom molecular dynamics simulation. With an eye toward testing how changes in the substrate surface may affect the choice of preferred orientation sites, several different combinations of substrate potential (Lennard-Jones wall, Lennard-Jones particles, and Embedded Atom Method metal) and variations in substrate surface-atom mobility were tested to understand how these factors alter the substrate surface
structure and whether subtly changed surface structure can produce significant alterations in adsorption at the metal-liquid interface.

The results of our simulations suggest that the modifications to the substrate potentials produces some noticeable but modest changes in the structure and ordering of methane and chloromethane adsorbed on the surface. Mass density profile calculations suggest that in all simulations, ordered layers form near the substrate surface with broadly similar peak density values, decaying toward the liquid-vacuum interface to roughly equal density values at approximately the bulk density. One slight exception to this was seen for methane on the embedded atom method (EAM) molybdenum, which showed more discernible layers approaching the vacuum interface and seemed to exhibit less pronounced decay in peak density away from the surface. A possible explanation is that the EAM molybdenum surface imposed slightly more order on each of the layers propagating through the adsorbed methane, which was not true for chloromethane. At each temperature simulated and for each substrate potential used, density profiles for chloromethane remained relatively similar with the exception of significant surface density enhancement on the mobile Lennard-Jones substrate, the cause of which is not immediately clear.

In the case of molecular orientation in the layer(s) near the substrate surface, differences in packing and orientation can be attributed to two types of substrate potential. On the Lennard-Jones wall, we see packing for both methane and chloromethane similar to what has been seen in previous work[134, 135, 162] for methane derivatives on graphite: symmetric molecules such as methane settle into a hexagonal, close-packed arrangement with a high degree of positional
order at the temperatures studied, while chloromethane appears to seek such a positionally ordered arrangement and becomes frustrated due to molecular asymmetry, orienting with the C-Cl bond nearly parallel to the substrate surface. On the atomistically-modeled molybdenum substrates, methane appeared to pack into very similar ordered structures at low temperatures, although the positional order seen in the radial distribution functions was not immediately recognizable. Chloromethane exhibited no such ordered arrangement; while the molecules again tend to orient with C-Cl bond nearly parallel to the surface plane, the molecules themselves showed no discernible positional order on these substrates.

In our opinion, the most interesting result originated with the estimation of the energy of binding between the adsorbate molecules and the substrate, calculated as a function of the substrate potential/mobility combination and the adsorption site on the surface of the molybdenum. Atomistically-modeled substrates had categorically higher binding energies compared to their Lennard-Jones wall counterparts, which may be expected because wall structures have no specific sites which become energetically favorable or unfavorable for binding. Between the atomistic substrates, however, preferences arise in the specific sites to which methane and chloromethane adsorb. Sites in the middle of a unit-cell face were most preferable for methane molecules, and within this group, molecules adsorbing on an immobilized Lennard-Jones molybdenum surface had the most favorable binding energies; EAM molybdenum binding sites were least preferable for these molecules. In the case of chloromethane, however, preference shifted to sites between two adjacent molybdenum atoms, the so-called "bridge" site; here, the
EAM and immobilized Lennard-Jones substrates saw, in general, greater binding energies than the mobile Lennard-Jones substrate.

The choice of binding site seems to be at least partially related to the geometry of the molecule and of the surface. On immobilized Lennard-Jones substrates, a perfectly ordered square lattice of molybdenum atoms is presented to the molecules. Methane, with its high degree of symmetry, may be favorite for choosing sites in the middle of a molybdenum unit cell face in order to maximize the number of molybdenum atoms with which it can interact. Chloromethane, however, with a large, asymmetric molecule that has a clear orientation axis along the C-Cl bond vector, appears to prefer sites in which it can place the CH$_3$ side of the molecule on one side of the "bridge", with the large chlorine side of the molecule on the other, perhaps to maximize the amount of interaction for both sides of the molecule with the surface, or perhaps to maintain the C-Cl bond vector orientation previously seen with polar methane derivatives on flat substrates.

This presents the central result of the preceding work: the molecules used as the adsorbates are small and have a limited number of configurations with which they can adsorb to a surface, and the surface itself varies from a perfectly flat, immobile surface to an atomically corrugated yet still-immobile surface, to a surface with both atomic-level features and surface mobility (itself limited to simple atomic vibrations around the crystal positions). The changes represented by those shifts in molecular orientation or surface structure are often thought of as minimal or appropriate for approximation by small pseudo-atom adsorbates or inflexible atomic arrays as substrates. However, what we feel we have been able to illustrate in this study is that these minor variations in orientation of
simple molecules and relatively small changes in the substrate surface structure can lead to differences in binding affinity for even these simple systems. This should have important implications for complex systems, especially for biomolecules such as proteins, in which individual segments of adsorbing sequences may each be affected by both the orientation of the adsorbing group and the local substrate surface structure. Then, when the total of these sequential group adsorptions are combined into the overall polypeptide or protein adsorption profile, small changes in adsorbate group orientation or substrate structure may elicit important information for accurate modeling of realistic systems.
CHAPTER IV
STRUCTURAL REARRANGEMENT AND TENSION
ACCUMULATION/AMPLIFICATION IN TETHERED BOTTLE-BRUSH
POLYMER LAYERS: COARSE-GRAINED MOLECULAR DYNAMICS
SIMULATION

4.1 Simulation Details

The coarse-grained force field used in this part of the simulation is essentially the bead-spring model popularized by Kremer and Grest[123, 124]. In this model, interparticle interactions between all pairs of beads are represented by a truncated and shifted Lennard-Jones 12-6 potential:

\[
U_{\text{LJ}}(r) = \begin{cases} 
4\epsilon_{\text{LJ}} \left[ \left( \frac{\sigma_{\text{LJ}}}{r} \right)^{12} - \left( \frac{\sigma_{\text{LJ}}}{r} \right)^{6} \right] + C & r \leq r_c \\
0 & r > r_c 
\end{cases}
\]

where \( r \) is the interparticle distance, \( \epsilon_{\text{LJ}} \) and \( \sigma_{\text{LJ}} \) represent the well depth of the interaction potential and bead diameter, respectively, and \( C \) is a constant which represents the shift in the potential to ensure continuity at the cutoff. In the current simulations, all nonbonded interactions are identical, implying the backbone and side-chains are chemically identical; accordingly, we have set \( \epsilon_{\alpha\beta} = \epsilon \) and \( \sigma_{\alpha\beta} = \sigma \) and have chosen our reduced units such that \( \sigma = \epsilon = m = 1 \) (the Boltzmann constant \( k_B \) is also set to 1). The Lennard-Jones potential is truncated at the minimum of the potential, \( r_c = 2^{1/6} \sigma \), which limits interparticle
interactions to pure repulsion, describing an essentially athermal model (i.e., very good solvent).

Polymer connectivity is achieved via the inclusion of a finitely extensible nonlinear elastic (FENE) potential between adjacent beads in the backbones and side chains:

\[ U_{\text{FENE}}(r) = \begin{cases} 
-\frac{1}{2}kR_0^2 \ln \left[ 1 - \left( \frac{r}{R_0} \right)^2 \right] & r < R_0 \\
\infty & r \geq R_0 
\end{cases} \]

where \( k \) is the FENE force constant and \( R_0 \) is the maximum extension of the bond. The standard choice for these parameters are taken from Kremer and Grest \((k = 30\epsilon/\sigma^2 \text{ and } R_0 = 1.5\sigma)\) for use in this study. With this set of parameters, competition between the repulsive Lennard-Jones potential and the FENE spring potential gives an equilibrium bond length of \( \approx 0.97\sigma \).

In the simulation of the tethering of bottle-brushes to a substrate, the substrate of choice for this phase of the simulation is the same Lennard-Jones 9-3 wall introduced in the preceding section on all-atom simulation. In this case, the cutoff of the wall potential is the potential minimum, \((z_c = \sqrt[3]{\frac{2}{3}}\sigma)\), as the primary function of the wall substrate in this set of simulations is to prevent adsorption of the bottle-brushes along the surface in order to create the surface confinement necessary to generate intramolecular tension within even isolated bottle-brushes. A Lennard-Jones wall with a cutoff that includes both attractive and repulsive interactions but that interacts only very weakly with the bottle-brushes could also be used for the same purpose, but we felt that a short-range repulsive interaction
coupled better to the purely repulsive interactions used in this form of the bead-spring model.

Our investigation centers on three main parameters: bottle-brush backbone length in terms of the number of coarse-grained backbone beads $N_{bb}$, side-chain length in terms of the number of coarse-grained side-chain beads $N_{sc}$, and the density of bottle-brush polymers grafted to the surface, referred to as the coverage $\Sigma$, given in the number of chains per unit surface area ($\sigma^{-2}$). Four different backbone lengths were chosen $N_{bb} = 50, 100, 150$ and 200 beads with one additional bead to serve as the site of attachment to the substrate. Three different side-chain lengths $N_{sc} = 50, 100$ and 200 beads were used for each of the backbone lengths, leading to a set of 12 basic bottle-brush molecules. The grafting density of side chains was set at one side chain per backbone unit in order to mirror the type of bottle-brushes created through macromonomer-based approaches seen in a number of recent studies[9–13]. Thus the total number of side chains for each molecule is equal to $N_{bb}$. Throughout the rest of this article, the molecules will be referred to by their side-chain and backbone lengths as ”$N_{sc} : N_{bb}$”; e.g., ”50:150” referring to the bottle brush with $N_{sc} = 50$ and $N_{bb} = 150$. For each of the 12 bottle-brushes constructed, a series of simulations was performed for molecular coverage ($\Sigma$) ranging from 0.00001 chains/$\sigma^2$ to 0.01 chains/$\sigma^2$, although the specific range of $\Sigma$ for each $N_{sc}:N_{bb}$ may vary; for example, for large $N_{sc}$ and $N_{bb}$, the total number of monomers precluded simulations at the high end of the range because the resultant monomer density became unfeasible. Similarly, for low $N_{sc}$ and $N_{bb}$, test simulations at low $\Sigma$ showed little to no variation in any of the properties examined.
Each simulation system was composed of 40 bottle-brush chains in a square-base simulation box (length = \((N/\Sigma)^{1/2}\), height equal to twice \(N_{bb}\) to accommodate any stretching) with periodic boundary conditions in the lateral directions. Initially, bottle-brushes backbones were generated in a standing-brush configuration and side chains were generated as random paths originating at the backbone. This resulted in possible monomer overlaps which would create numerical instabilities if the Lennard-Jones interaction was used immediately. In order to remove overlaps, we first subjected systems to a short period of simulation in which the interparticle potential was represented by a soft-core cosine potential (similar to that used in Auhl et al.[163] for the equilibration of long-chain melts) that increased in strength. Within a short simulation time (on the order of 100,000 time steps), the "push-off" potential removed overlaps sufficiently that the Lennard-Jones potential could then be included without instability.

Tethering the bottle-brush backbones to the surface was done by attaching the backbones to a "dummy" bead, positioned at the substrate surface, to act as the point of attachment or tethering site. Immobilizing this tethering bead results in a bottle-brush that is fixed at the surface, with the tether representing a covalent bond to the substrate or attachment group. Allowing the tethering site to move along the plane of the substrate but not outside of it represents a non-covalent interaction which allows lateral movement the bottle-brush. We refer to each of these cases as "fixed" or "mobile" tethers, respectively, and performed either full series or test simulations on three different variations: fixed tethers randomly placed on the substrate, fixed tethers arranged in a hexagonal lattice on the substrate, and mobile tethers initially placed randomly. Apart from minor
variations within the error of the simulation, we found no significant difference in the simulation results based on the choice of tethers, thus — unless otherwise specified — the data contained herein refers to the case of mobile tethers.

All simulations were performed using the LAMMPS simulation package, using a velocity-Verlet algorithm to integrate the equations of motion. In the bead-spring model used here, the beads are considered as effectively very large particles moving in a continuum of much smaller particles, for which Langevin dynamics describes the system sufficiently; the particles are therefore coupled to a "Langevin thermostat", and the equation of motion for a particle $i$ in our simulation system is given by a Langevin equation:

$$m_i \frac{d^2 r_i}{dt^2} = -\nabla U_i - m_i \gamma \frac{dr_i}{dt} + W_i(t)$$

where the second term represents a friction term (with damping constant $\gamma$) and $W_i$ is a Gaussian noise term which can be related to the damping constant by the fluctuation-dissipation relation:

$$\langle W_i(t)W_j(t') \rangle = 6m_i \gamma k_B T \delta_{ij} \delta(t - t')$$

It is often suggested that if the goal is to maintain a constant temperature, the value of the damping constant $\gamma$ should be kept small, as large $\gamma$ will provide sufficient randomness to help explore the phase space but can result in large temperature deviations. It was also shown by Tsige and Grest[164] that the choice of $\gamma$ can affect the self-diffusion coefficients in bead-spring systems, which suggests the choice of $\gamma$ can have an effect on particle dynamics. What is not
known and rarely discussed is how small is "small" when discussing $\gamma$. Most commonly, simulations using the bead-spring model detailed here give a value of $\gamma = 0.5 \tau^{-1}$, where $\tau = (m\sigma^2/\epsilon)^{1/2}$ is the characteristic time scale of the bead-spring simulation. The choice of $\gamma$, appears to be largely a matter of convention, however, as early simulations[123] tested a range of values from 0.5 to 1.5 $\tau^{-1}$ and the aforementioned work by Tsige and Grest went even further before instability caused significant issues. In our simulations, two values of $\gamma$ were tested: 0.5 $\tau^{-1}$ and 2.0 $\tau^{-1}$. Both were shown to maintain a constant temperature for the simulations with minimal fluctuations, and there was little difference noted between the brush-layer structure after the initial equilibration process.

Thus, the simulations presented herein were performed in a constant volume/constant temperature ensemble with $T = 1$. For an athermal model, this is a convenient choice of temperature, but modest variations in temperature are not expected to alter behavior significantly. A time step of $\delta t = 0.005\tau$ was used for all simulations. Equilibration runs were performed for a period of 125,000$\tau$ or more with observations made of system energy, whole-molecule radius of gyration ($R_g$) and brush side-chain $R_g$ and end-to-end distance $R_{ee}$ until the brush conformations were seen to stabilize. At the end of this equilibration period, the runs were extended by more than 20,000$\tau$, with analysis being performed over 100 configurations. A schematic of the final configuration seen in one of the cases (50:200, $\Sigma = 0.0008$ chains/$\sigma^3$) is shown in Figure 4.1 as an example of the structures obtained.
4.2 Results and Discussion

One of the key considerations in work by Sheiko et al.[110, 111] is the classification of bottle-brushes as “hairy” or “crew-cut”. Hairy bottle-brushes are those for which the effective diameter (D) of the brush is much larger than the contour length of the backbone (L), which causes hairy bottle-brushes to more often adopt star-like conformations. For crew-cut brushes, \(D \ll L\), and crew-cut brushes more often adopt cylindrical conformations (see Figure 4.2). For the backbone tension, their analysis suggests that one of the main differences between the two classes of bottle-brushes is in how and where backbone tension develops in a single bottle-brush molecule, unperturbed by neighboring bottle-brushes. In both cases, the backbone tension is the sum of the tensile forces originating in the side chains and thus is minimized at the backbone free end and increases with increasing distance from it. However, their analysis also shows that this increase in backbone tension has a limit: backbone tension is only expected to
increase in regions where the backbone length is smaller than the lateral size of the bottle-brush, i.e., where the bottle-brush can be modeled as a star-like molecule. For hairy bottle-brushes, this is the entire length of the brush; tension increases from the free end of the backbone to the substrate surface. In crew-cut bottle-brushes, however, when the distance from the free end becomes comparable to the brush width, the increase in backbone tension reaches a constant value and remains there. This effectively divides a crew-cut brush into two sections: a hairy-like focusing section, where tension amplification takes place and a transmission section, where the accumulated backbone tension neither decays nor accumulates.

This further implies that as long as one examines isolated bottle-brush molecules, tension accumulation in hairy bottle-brushes is primarily a function of the number of side chains and not their degree of polymerization, while tension accumulation in crew-cut bottle-brushes is dependent on the size of the focusing region, which is dependent on the side-chain degree of polymerization.

Figure 4.2: Representations of a hairy bottle-brush molecule (a) with backbone length $N_{bb}$ and side-chain length $N_{sc}$, as well as a crew-cut bottle-brush molecule (b), showing the difference in the lateral size of the molecule (called $R$ in ref. [111] but referred to in the text as $D$) vs. the contour length of the backbone, $L$. Adapted with permission from ref. [111]. Copyright 2011 American Chemical Society.

Thus, to begin the discussion of tension accumulation for the 12 molecules (combinations of three side-chain and four backbone lengths), we calculated the effective cross-section diameter $D$ of the bottle-brushes, the backbone contour
length $L$, and the ratio $D/L$, which gives an indication of whether the bottle-brushes are hairy, crew-cut, or in the transition between the two. This data is presented in Table 4.1. Note that the effective brush diameter is given as $D$, instead of $R$ as in reference [111]. Both give similar indications of the lateral area presented by the bottle-brushes, but $D$ may be more useful in comparisons to the inter-brush distance $d$, given as the average distance between nearest-neighbor tethering beads.

Table 4.1: Comparison of average brush diameter ($D$), average backbone contour length ($L$) and ratio $D/L$ for isolated bottle-brushes used in study. Error in $D$ and $L$ is on the order of 0.1 $\sigma$

<table>
<thead>
<tr>
<th>$N_{bb}$</th>
<th>$N_{sc}$</th>
<th>D</th>
<th>L</th>
<th>D/L</th>
<th>$N_{bb}$</th>
<th>$N_{sc}$</th>
<th>D</th>
<th>L</th>
<th>D/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>30.9</td>
<td>48.8</td>
<td>0.63</td>
<td></td>
<td>50</td>
<td>30.4</td>
<td>146.4</td>
<td>0.21</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>50.1</td>
<td>48.8</td>
<td>1.03</td>
<td>150</td>
<td>100</td>
<td>49.3</td>
<td>146.6</td>
<td>0.34</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>77.6</td>
<td>48.9</td>
<td>1.59</td>
<td></td>
<td>200</td>
<td>81.2</td>
<td>147.0</td>
<td>0.55</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>30.5</td>
<td>97.6</td>
<td>0.31</td>
<td></td>
<td>50</td>
<td>30.2</td>
<td>195.2</td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>49.9</td>
<td>97.7</td>
<td>0.51</td>
<td>200</td>
<td>100</td>
<td>49.5</td>
<td>195.5</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>79.8</td>
<td>97.9</td>
<td>0.82</td>
<td></td>
<td>200</td>
<td>79.6</td>
<td>196.1</td>
<td>0.41</td>
<td></td>
</tr>
</tbody>
</table>

The data in Table 4.1 suggest that the majority of the bottle-brushes constructed for this study should be classified as crew-cut, as the contour length exceeds the unperturbed bottle-brush diameter by a factor of two or more in most cases. Two cases with the longest side chains and shortest backbones — 100:50 and 200:50 — show cross-section diameters comparable to the contour length or larger than the contour length, suggesting these cases may either be considered "hairy" brushes or within the transition between brushes.

In Figure 4.3, we first explore the general trends in tension accumulation by plotting the backbone tension for several values of $\Sigma$ in one specific case (100:100) vs. the bond index. Here, the bond index represents the position of a backbone bond along the backbone; low indices represent bonds near the wall
surface and increasing indices represent bonds further along the backbone, moving toward the free surface. Here we can see that at low coverages, the backbone tension appears nearly constant throughout the brush, increasing slightly at the wall surface, likely from the constraining presence of the wall, and decreasing to a low but non-zero tension at the free surface (this value, the "intrinsic" backbone tension, has a value in the range of 3 to 4 $\epsilon/\sigma$ in all cases). From the theory for crew-cut brushes, the near-constant tension region in the interior of the backbone is representative of the expected transmission region, although careful inspection suggests that in the simulated brushes, there is a small accumulation of tension throughout this transmission region, suggesting that while tension accumulation is low here, it cannot be neglected entirely.

Increasing the coverage, the brushes begin to become crowded, and the tension in the backbone is no longer nearly constant. Instead, the backbone tensions at higher coverages in Figure 4.3 suggest a rapid increase in tension away from the free surface that begins to saturate close to the wall. A possible explanation here is that as the coverage increases, the region of maximum tension generation near the free surface grows and more tension accumulates within this region. In this case, the size of the focusing and transmission regions in crowded brushes may be related to the degree of crowdedness, and may suggest that side chains in crowded layers are reoriented, which would result in a much larger region of backbone tension accumulation.

To examine the effects of the dense grafting of bottle-brush molecules to a substrate, it is important to understand the different "regimes" of tension accumulation and amplification expected with increasing molecular coverage $\Sigma$ or,
Figure 4.3: Average backbone tension as a function of bond index, where lower indices represent bonds close to the wall and higher indices represent bonds closer to the free surface. Tension increases with increasing coverage, $\Sigma$, as suggested in the figure.

equivalently, decreasing inter-brush spacing $d$. In the theoretical analysis of tension generation in hairy bottle-brushes, Panyukov et al.[111] distinguished between three such regimes based on the inter-brush spacing: the isolated-brush regime, the loose-grafting regime and the dense-grafting regime. Although the extension to crew-cut bottle-brushes is not necessarily obvious, the basis upon which the distinctions are made can easily be extended to the crew-cut cases. The first of these, the isolated-brush regime, exists when the spacing between brushes is greater than the lateral dimensions of the brushes ($d > D$), such that the short-range interactions of the bead-spring model imply that neighboring bottle-brushes do not directly interact with one another. Thus, the structure of the brush and the accumulation of any tension within the brush is the effect of intramolecular interactions involving side chains on the same backbone, i.e. the steric repulsion.
between densely grafted side chains that is responsible for the extended conformations we see in Figure 4.1 and which is responsible for the self-generation of tension within the bottle-brush backbone.

When $\Sigma$ is large enough that the distance between bottle-brushes is less than the lateral size of the bottle-brush ($d < D$), side chains begin to overlap. In the analysis of hairy bottle-brushes, coverages greater than this cutoff are further subdivided into two categories: the loose-grafting regime ($L < d < D$) and the dense-grafting regime ($L > d > z^{1/2}b$, where $z$ is the number of side chains of the bottle-brush). In the loose-grafting regime, overlap between the side chains of neighboring bottle-brushes is limited to a region outside the central core of the bottle-brush. For hairy brushes, we estimate this to be within a radius $r$ on the order of the backbone contour length (which, for hairy bottle-brushes, is less than the bottle-brush diameter) and as such does not perturb the portions of the side chains within the core region. The result is no increase in backbone tension. In the dense-grafting regime, most of the brush is affected by the overlap between side chains, except for an end-cap region near the backbone free end whose size is dependent on $d$ and thus $\Sigma$. As the size of this end-cap region decreases, the tension throughout the remainder of the backbone increases until reaching the limit of molecular coverage ($\Sigma_{lim} \approx z^{1/2}b$). At this coverage, all side chains are deflected perpendicular to the substrate and pack akin to a dense brush of linear polymer chains.

It is not currently known whether such three-regime behavior could also be assumed for crew-cut bottle-brushes like those in the current study. It is clear one should expect a transition from an isolated-brush regime to one where the
side chains of neighboring bottle-brushes overlap and that this crossover should take place for \( d \) on the order of the bottle-brush cross-section diameter, but it is not clear, once neighboring brushes begin to overlap, whether parts of the brush should be affected first or whether the entire bottle-brush will be affected. Once \( \Sigma \) is large enough that side-chain overlap is an issue, crew-cut bottle-brushes may not have the same depth of a “loose-grafting” regime, as the small diameter of a crew-cut brush (relative to hairy bottle-brushes) may suggest that side-chain overlap between crew-cut bottle-brushes perturbs the core of the brush structure almost immediately.

The first method we used to correlate changes in the side-chain conformations with variation in the molecular coverage was to calculate the moment of inertia tensor of the side chains. The tensor can be diagonalized to give three eigenvalues \( \lambda_1 > \lambda_2 > \lambda_3 \). The sum of the three eigenvalues equals the radius of gyration, \( R_g^2 = \lambda_1 + \lambda_2 + \lambda_3 \). The ratios of the eigenvalues can be used to describe the shape of the side chains and used to determine the asphericity, acylindricity or relative shape anisotropy[165]. Calculation of the relative shape anisotropy of the backbones suggests they maintain a high degree of linearity, even at low coverage, regardless of \( N_{sc} \) or \( N_{bb} \). The mean square radius of gyration of the side chains, averaged over all side chains in the system, is plotted in Figure 4.4 as a function of the coverage.

In Figure 4.4, we see indications of a similar three-regime behavior for the crew-cut brushes as was suggested for hairy brushes in the scaling analysis (three regimes outlined in the sketch in Figure 4.5). In each case, there is a regime at low \( \Sigma \) in which \( \langle R_g^2 \rangle \) is essentially constant, suggesting that the side-chain \( \langle R_g^2 \rangle \) is
Figure 4.4: Mean square radius of gyration \( \langle R_g^2 \rangle \) of side chains versus coverage for \( N_{sc} = 50 \) (left), 100 (middle) and 200 (right), independent of coverage. From the point at which \( \langle R_g^2 \rangle \) begins to increase, we can estimate the isolated-to-overlapping transition. Analyzing the relationship between \( \Sigma \) and the inter-brush spacing \( d \) \((\Sigma \approx 1/d^2)\), the transition for \( N_{sc} = 50 \) \((\Sigma \approx 0.001 - 0.002\sigma^{-2})\), \( N_{sc} = 100 \) \((\Sigma \approx 0.0006 - 0.0008\sigma^{-2})\) and \( N_{sc} = 200 \) \((\Sigma \approx 0.0002 - 0.0004\sigma^{-2})\) correspond to values of \( d \) in the range of 20-27 \( \sigma \), 31-37 \( \sigma \) and 41-58 \( \sigma \), respectively, which correspond to the expected transition point \((d \approx D)\) for the isolated-brush to side-chain overlap transition.

Figure 4.5: Simplified sketches of the three coverage regimes described in theory (ref. [111]) for hairy bottle-brushes and suggested by \( \langle R_g^2 \rangle \) for crew-cut brushes in this study. In (a), the interbrush spacing \( d \) is much greater than the unperturbed brush diameter \( D \), and the conformations of the side chains are essentially determined by intramolecular interactions between side chains on the same bottle-brush. In (b), \( d \leq D \), such that side-chain overlap occurs at the edges between neighboring bottle-brushes. A lack of entanglement suggests that side chains may reorient rather than interpenetrate. In (c), \( d \ll D \), such that side-chain overlap between neighboring bottle-brushes dominates the conformations available to the side chains.
At coverages above the first transition as $d$ decreases below $D$, $\langle R^2_g \rangle$ exhibits a noticeable decrease from its value in the isolated-chain regime. The level of decrease in $\langle R^2_g \rangle$ appears to be at least partially dependent on $N_{bb}$, but the inter-brush spacing/coverage at which the depression in $\langle R^2_g \rangle$ begins is not dependent on $N_{bb}$. This decrease in $\langle R^2_g \rangle$ suggests a possible compression or reorganization of the side chains as they begin to overlap. With increasing $\Sigma$/decreasing $d$, however, the value of $\langle R^2_g \rangle$ begins to fall and reaches a minimum at what may be the transition from a loose-grafting or weak partial overlap regime to a marked increase in $\langle R^2_g \rangle$ as the molecular crowding increases, suggesting a dense-grafting or strong overlap regime in which side chains stretch, necessitating a reorientation as the free volume decreases.

While the position of the transition from isolated bottle-brushes to partial side-chain overlap is clear, the position and nature of the transition between the putative loose-grafting and dense-grafting regimes cannot be estimated from Figure 4.4 alone and clearly cannot be based on the same criteria as for hairy bottle-brushes. However, an approach similar to the scaling arguments for hairy bottle-brushes offers some insight. In the dense-grafting regime, as long as the inter-brush distance remains lower than the physical limit of chain packing, a portion of the brush near the free end of the backbone will remain unperturbed by the presence of neighboring bottle-brushes. As $d$ increases, the unperturbed region grows. At the crossover to the loose-grafting regime, the distance from the free end $s$ to the point where the crossover takes place ($r^* \approx \frac{d^2}{L}$) reaches a maximum (at $d = L$, $s \approx r^* \approx L$, and the brush enters the regime where a cylindrical core region around the backbone is unperturbed, i.e., the loose-grafting regime). Thus at
or near the crossover from the loose-grafting regime to the dense-grafting regime, the first part of the bottle-brush backbone to be significantly affected by tension amplification due to neighboring chains is the linker, and the linker tension should show a distinct increase at the crossover.

Figure 4.6: Average tension at surface as a function of coverage $\Sigma$ for $N_{sc} = 50$ (left), 100 (center) and 200 (right), for the four values of $N_{bb}$ given in the inset. Note logarithmic horizontal axis.

Thus, a model that gives an expression for the linker tension as a function of coverage, including a crossover parameter that describes the loose- to dense-grafting transition in terms of small-to-large deviation from an intrinsic linker tension could offer not only a method for evaluating the relationship between the transition from loose-grafting to dense-grafting, but also a way to characterize the intrinsic linker tension in the limit of near-zero coverage (essentially, the single-brush limit). After evaluating the relationship between linker tension and coverage as seen in Figure 4.6, the expression that most accurately models the linker tension data is

$$f_{\text{link}}(\Sigma) = T_0 \left[ 1 + \left( \frac{\Sigma}{\Sigma^*} \right)^\beta \right]$$  \hspace{1cm} (4.1)
where $T_0$ represents the intrinsic linker tension in the single-brush limit, $\Sigma^*$ represents the low- to high-tension transition coverage, and $\beta$ represents a scaling exponent. Values for $\Sigma^*$ are plotted, with error bars relating to a 95% confidence interval, in Figure 4.7. In Figure 4.7, it is apparent that this crossover coverage varies primarily with $N_{sc}$, although for short backbones, which may be in transition from crew-cut to hairy bottle-brushes, a slight increase in $\Sigma^*$ can be seen.

**Figure 4.7:** Estimates from fitting to Eq. 1 of the crossover coverage $\Sigma^*$ vs. $N_{bb}$ and $N_{sc}$ as an estimate of loose-grafting to dense-grafting transition. Vertical bars signify 95% confidence intervals from the fitting procedure.

For each regime, the extent or lack of side-chain overlap will have differing effects on the backbone tension. In the isolated-brush regime, the scaling analysis provides relationships to describe the backbone tension in crew-cut bottle-brushes, which will allow us the opportunity to compare our findings with the assumptions inherent in such a scaling relationship. In the case of the identified loose-grafting and dense-grafting regimes, for crew-cut brushes the overall picture is not as clear. Thus, in the next sections, results for the backbone tension and side-chain conformation in each of the three regimes will be presented to determine how well our
simulation model matches the established theory and how well it might extend to densely grafted bottle-brush layers.

4.3 Results: Isolated-Brush Regime

In the theoretical analysis by Panyukov et al.[111], the backbone tension in both hairy and crew-cut bottle-brushes is dependent on the distance \( s \) from the free end of the bottle-brush backbone. In both cases, the tension due to the side chains at any distance \( s \) from the free end is the sum of individual side-chain forces acting within this end-cap region, and within this end-cap, the total force exerted on the backbone at distance \( s \) can be modeled as the tension in a spacer of length \( s \) tethering a star polymer to an imaginary substrate at distance \( L - s \) from the real substrate (see Figure 4.8). The star polymer used to model the tension in this case is a \( z_s \)-arm star, where \( z_s \) is the number of side chains attached to the backbone within \( s \) of the free end. Thus, if the grafting density of side chains is \( m \) (i.e., \( m \) side chains per backbone monomer), the star-like end-cap of the bottle-brush molecule has a \( z_s = ms/b \) arms, where \( b \) is again a typical Kuhn length for the model polymer (on the order of \( \sigma \) for the simulations herein). In the theoretical treatment and the simulations here, \( m = 1 \), so \( z_s = s/b \). In the same article, the authors give the expression for the tension in the spacer of a \( z_s \)-arm star polymer (in a solvent environment, as opposed to the melt state) as \( f \approx k_BT \frac{z_s^{3/2}}{h} \), where \( h \) is the length of the spacer. With \( h = s \) and \( z_s = s/b \), the tension at a distance \( s \) from the bottle-brush free end is \( f(s) \approx f_0 \sqrt{s/b} \), where \( f_0 \approx k_BT/b \) is the intrinsic tension in an average polymer chain (\( f_0 \) is roughly on the order of a piconewton, assuming \( T = 300 \) K and \( b \approx 1nm \)).
Figure 4.8: Schematic of bottle-brush molecule in the isolated-brush regime showing the theoretical derivation of backbone tension. In theory, the tension in the backbone at a distance $s$ from the free end (and thus a distance $L - s$ from the tethering site) is equivalent to the tension in a star polymer tethered at a distance $L - s$ from the real substrate. The tension in the "tethered star" is then due to the sum of the forces exerted by the side chains grafted to the "tethered star." Adapted with permission from ref. [111]. Copyright 2011 American Chemical Society.

The above is expected to hold for both hairy and crew-cut bottle-brushes, with the caveat that the maximum extent of the star-like end-cap region is a distance $s$ from the free end less than the width of the brush. For hairy bottle-brushes this is not an issue; by definition, a hairy bottle-brush must have contour length $L \ll D$. The maximum tension in the backbone is found at the "linker" site that tethers the brush to the substrate. Using $L = z b$ (with total number of side chains $z$ and assuming $m = 1$), the linker tension for a hairy bottle-brush is given as $f_{\text{link}} \approx f_0 \sqrt{z}$.

In a crew-cut bottle-brush, however, $L \gg D$, thus the tension only increases in the end-cap region for $s < D \approx N_{sc}^{3/4} b$. This is the definition of the focusing region of a crew-cut bottle-brush; a hairy bottle-brush is essentially en-
tirely a focusing region. If one assumes that the accumulation of tension in the crew-cut backbone is due to the star-like end-cap up to \( s = N_{sc}^{3/4} \), the maximum tension in a crew-cut bottle-brush, located at the base of the end-cap region, can be found from the same expression for the tension \( f(s) \) at a distance \( s \) from the free end of a hairy bottle-brush; the result is \( f_{max} \approx f_0 N^{3/8} \). Under the assumptions of this model, this is the tension at any point along the backbone between \( s \) from the free end and the substrate. No tension is expected to accumulate in the transmission region between the end-cap and substrate, neither does it attenuate with distance; the "transmission" region can be thought of as a conduit that delivers a constant tension at any point on the backbone within it.

Figure 4.9: Average backbone bond tension as a function of the bond index for three series of simulations of comparable overall system size. Lower indices indicate bonds closer to the tethering point. Each graph contains several plots for values of \( \Sigma \) indicative of isolated bottle-brushes for each molecule configuration.

With this theoretical model in hand, we can examine our simulation data for the isolated-brush regime. In Figure 4.9, we plot the average bond tension in individual backbone bonds as a function of the bond index for three representative bottle-brush configurations: short SCs/long backbones (50:200; highly crew-cut), long SCs/short backbones (200:50, between crew-cut and hairy), and one case in between (100:100, suggested from Table 4.1 as crew-cut). The bond
index represents each bond within the backbone; smaller bond indices represent bonds near the substrate, while larger ones represent bonds near the free end. Qualitatively, the plots have three distinct regions: a region near the free end of tension increasing as one moves away from the free surface, characteristic of the focusing region; a plateau region in the interior of the brush, characteristic of the transmission region, and a region near the substrate in which the tension increases very slightly. The latter region is not expected from the theoretical models and may be the result of confinement of the side chains near the surface due to the presence of the substrate.

Another qualitative difference among the tensions in Figure 4.9 is the presence of an increasing tension within the transmission region for systems with longer side chains and shorter backbones. For the (50:200) case, which is expected to behave most like a crew-cut bottle-brush, the majority of the transmission region shows little or no change in the tension aside from minor fluctuations and tension values within this region that appear independent of coverage until the highest isolated-brush coverage shown (\(\Sigma = 0.002\text{chains}/\sigma^2\)), whereas tension in the (200:50) systems appears to increase almost linearly from the free surface to the substrate surface.

Quantitatively, a comparison to the theoretical model can be made by calculating the average transmission-region bond tension, as the tension throughout the transmission region should be essentially constant. Assuming a power-law relationship, \(f = f_0N_{sc}^\xi\), we obtain a value for the exponent of \(\xi = 0.34 \pm 0.05\), close to but less than the 0.375 expected from the scaling analysis. This discrepancy is also noted if one uses the data in Figure 4.1 to determine the relationship
between the diameter of the bottle-brush molecules (calculated in the isolated-brush regime) and $N_{sc}$. A similar power-law relationship, $R_{CS} \approx N_{sc}^\nu$ is expected with $\nu = 3/4$ if we assume that the side chains assume conformations of a two-dimensional or quasi-two-dimensional nature; if the side chains instead exhibit three-dimensional self-avoiding walk behavior, the exponent should be equal to the Flory exponent, $\nu = 0.588$. In our case, from the data in Figure 4.1, we obtain a value of $\nu = 0.68 \pm 0.03$, which is again far from the $3/4$ exponent expected for the 2D-SAW model, but closer to that expected for a 3D-SAW. This has been the subject of some debate, with the scaling analysis of Panyukov et al. and some simulations[113] reflecting the 2D behavior, while Rathgeber et al.[166, 167] note behavior closer to the 3D model. It has also been suggested[168] that the $3/4$ dependence may better reflect side chains on a rigid cylindrical backbone, which certainly appears to be the case in the earlier work of Murat and Grest. When the intrinsic flexibility of the backbone in normal polymers is considered, the exponent $\nu$ for bottle-brushes in good solvent is closer to the Flory exponent. Rathgeber et al. also suggest a possible argument in favor of changes being related to the flexibility of the bottle-brushes, noting that the entropy loss suffered by stretching a more flexible backbone could be easily made up by entropy gained in the numerous side chains which can shift from two-dimensional to three-dimensional behavior.

Earlier, we analyzed the crossover coverage from the model equation for linker tension as a function of the molecular coverage. The same model also gives us an estimate of the intrinsic linker tension at the limit of negligible coverage, which can be used to evaluate how the linker tension varies with $N_{sc}$ and $N_{bb}$. 
A graphical representation of these data is given in Figure 4.10, along with 95% confidence interval on each parameter obtained from the model fit.

Figure 4.10: Linker tension in single-brush ($\Sigma = 0$) limit as a function of $N_{bb}$ and $N_{sc}$ from fitting of linker tension data to Eq. 1; vertical bars on data points represent 95% confidence interval from model fit.

Qualitatively, the data in Figure 4.10 suggest that the intrinsic linker tension, as predicted for crew-cut brushes, is nearly independent of $N_{bb}$; while there appears to be an increase in $T_0$ for $N_{sc} = 200$ with increasing $N_{bb}$, for $N_{bb} = 100, 150$, the error bars suggest that this difference is unlikely to be statistically significant, which is also true of the fluctuations in $T_0$ with increasing $N_{bb}$ for smaller values of $N_{sc}$. At the same time, the dependence of $T_0$ on side-chain length is similarly weak in several cases, as extracting the exponent $\alpha$ from the power law $T_0 \approx N_{sc}^\alpha$ yields $\alpha = 0.16$ for $N_{bb} = 50$, 0.13 for $N_{bb} = 100$, 0.21 for $N_{bb} = 150$, and 0.30 for $N_{bb} = 200$, only the last of which is in line with expectations for the linker tension in crew-cut bottle-brushes (assuming $D \approx N_{sc}^{3/5}$ and not $N_{sc}^{3/4}$, as was suggested in the scaling analysis). The decrease in the scaling exponent with decreasing $N_{sc}$ may be explained by the nature of the bottle-brushes studied: while the majority of the bottle-brushes in this investigation can be classified as crew-cut (see Table 4.1), there is a notion of a transition from crew-cut behavior to hairy-like behavior as $N_{sc}$ decreases and $N_{bb}$ increases. Bottle-brushes with $N_{bb} = 50$ and $N_{sc} = 100$ or
200 may be thought of as transitional bottle-brushes or may even extend slightly into hairy bottle-brushes, where theory suggests the linker tension is independent of both $N_{bb}$ and $N_{se}$.

4.4 Results: Loose-Grafting and Dense-Grafting Regimes

Based on previous analysis, we have defined the loose-grafting regime as pertaining to brushes separated by a distance $d$ less than the diameter of the unperturbed brush, but greater than $N_{sc}^{1/2}b$. In the earlier discussion of the crossovers between pairs of the proposed three regimes, we noted the decreasing $\langle R^2_g \rangle$. Analysis of the principal moments of the gyration tensor can offer significant insight in this case into the changes in shape of many of the polymers.

A number of shape descriptors can be calculated using the principal moments of the gyration tensor. Of particular interest in this study are the asphericity, $B$, the acylindricity $c$ and the relative shape anisotropy, $\kappa^2$, defined in the following manner (using principal moments $\lambda_1 \geq \lambda_2 \geq \lambda_3$):

\[
B = \lambda_1 - \frac{1}{2}(\lambda_2 + \lambda_3)
\]

\[
c = \lambda_2 - \lambda_3
\]

\[
\kappa^2 = \frac{B^2 + (3/4)c^2}{R^4_g}
\]

In this analysis, the relative shape anisotropy $\kappa^2$ is a very useful quantity for quickly analyzing the average shape of the side chains. When $\kappa^2 = 0$, the molecule exhibits tetrahedral or higher symmetry, and when $\kappa^2 = 1$, the particles are arrayed in a perfectly straight line. Unperturbed linear chains show an average
\( \kappa^2 \) near 0.41[165]; molecules with slightly more spherical symmetry skew toward lower values, and stretched linear chains to higher values.

In the isolated-brush regime, the average \( \kappa^2 \) varies in the range from 0.2 to 0.3, suggesting a largely linear conformation for side chains, on average. In the loose-grafting regime, analysis of the principal moments of the gyration tensor show that \( \lambda_1 \) decreases significantly while \( \lambda_2 \) and \( \lambda_3 \) remain relatively constant. This is reflected in a reduction of \( \kappa^2 \) and the asphericity, suggesting the side chains in this regime are being compressed toward a more spherical distribution.

At the second crossover and beyond, when \( \langle R_g^2 \rangle \) begins to increase dramatically, \( \lambda_1 \) increases rapidly while \( \lambda_2 \) and \( \lambda_3 \) decrease significantly, shifting \( \kappa^2 \) to values of roughly 0.6-0.8, suggesting a significant increase in linearity; at the same time, acylindricity decreases significantly, suggesting the side chains become more rod-like in their extended conformations as evidence of reorientation and stretching.

Another way to view the stretching and deflection of side chains as a function of increased crowding is through examination of the side-chain end-to-end vector, specifically the component of the end-to-end vector normal to and away from the substrate surface. In Figure 4.11, we have plotted the average normal component of the end-to-end vector vs. the point of attachment for the side chains for the 100:200 bottle-brush system at coverages representing the isolated-brush, loose-grafting and dense-grafting regimes. The specific bottle-brush system in Figure 4.11 was chosen because the isolated-brush dimensions suggest this case falls well within the definition of a typical crew-cut brush, although the behavior seen in the figure is widely indicative of all of the bottle-brushes simulated.
In Figure 4.11, the lowest coverage (0.0001 $\sigma^2$) is within the isolated-brush regime and shows two zones of clear side-chain deflection: one within the upper 30 $\sigma$ of the backbone free end and one within the first 10-15 $\sigma$ of the substrate surface. In the former case, the deflection of side chains near the free end of the brush is to be expected as part of the focusing region of the crew-cut structure; tension is generated here by the extension of side chains toward the free volume at the brush surface. This upper deflection zone is common to all coverages, but the extent to which the deflection zone extends into the traditional transmission zone of the bottle-brush is greatly affected by the degree of molecular crowding. The lower deflection zone near the substrate is likely an effect of confinement of the side chains between the short-range repulsive surface and the steric repulsion of side chains above it on the backbone. In low-coverage situations, the amplitude of this lower deflection zone is greater than that of higher-coverage cases, likely because of the effect of crowding on the expansion of the upper deflection zone.
A small increase in coverage, to the loose-grafting regime ($\Sigma = 0.001 \text{ chains}/\sigma^2$) does not exhibit this expansion — aside from a slight enhancement of the magnitude of side-chain deflection near the backbone free end, the loose-grafting case and the isolated-brush case appear nearly identical (to within the error of the simulation). When the coverage is raised to the dense-grafting regime ($\Sigma > 0.002 \text{ chains}/\sigma^2$), the increased crowding between overlapping side chains causes more and more side chains further into the middle of the brush to reorient toward the free surface and to stretch to a greater extent. This increase in deflection carries with it the generation of tension further into the bottle-brush, beyond the classical transmission zone, as chain deflection and extension generate individual tension within an increasing number of side chains, transmitting increasing amounts of tension to the bonds along the backbone.

4.5 Conclusion

In this work, we have used coarse-grained molecular dynamics simulation to attempt to elucidate some of the factors affecting the appearance and nature of tension amplification in layers of bottle-brush polymers tethered to a flat, featureless surface, especially with regard to how tension develops as the crowding of chains at the tethering surface is varied, but also as the dimensions of the backbone and side chains are altered. In the first segment of the results, we discussed the tension specifically, outlining how increases in side-chain length correlate directly with the appearance of a value of the surface coverage at which tension amplification in the bottle-brush backbone first begins to appear. Below this coverage, tension is almost constant, as the average distance between bottle-brush polymers
remains larger than the lateral dimensions of the brushes, causing side chains to interact only with neighbors on the same backbone. Beyond this “cross-over” coverage, however, side chains of neighboring bottle-brush chains begin to interact significantly, and tension amplification becomes readily apparent.

In the second part of the results, we examined possible correlations between the dimensions of tethered bottle-brush polymers and the possible appearance of an intermediate phase between the single chains and crowded-brush regimes. A slight compression of the side chains, concurrent with small increases in the backbone tension, but with a lack of side-chain reorientation, suggest the possibility of interaction causing a “soft” repulsion of side chains until the crowding at the surface forces side chains to interact and reorient in order to avoid complications due to the effects of steric hindrance. These data and the proposed explanations should shed some light on the basic physical properties of this interesting polymer architecture and engender new and expanded research in the future.
CHAPTER V
FIRST IMPRESSIONS IN MULTIBLOCK TETHERED BOTTLE-BRUSH LAYERS

5.1 Simulation Details

In homopolymer simulations of tethered bottle-brush layers, there is only one set of interactions between particles and one set of parameters to describe the interaction strength and length scale. Thus, the athermal model used in Chapter 4 represents a system in which emergent characteristics are essentially of a purely physical nature; i.e., extending primarily from excluded volume interactions and not from any intrinsic chemical interactions. If one wants to include an approximation of chemical interactions, it is most fitting to examine a system in which at least two types of particles are present.

Even extending the number of particles in the simulation to just two creates a plethora of possible parameters that can be altered. One could envision a system of bottle-brushes built on two different types of backbone chemical species, although such bottle-brushes might be difficult to synthesize. On the other hand, "grafting-through" methods for polymerization have enabled a wide variety of species to be included on a single side chain, and have been used to create macromonomers composed of a linear polymer connected to a backbone building block, with the brush created by polymerization of the backbone units. Almost any form of linear polymer can be used to create these macromonomers,
such as block copolymers, alternating copolymers, and gradient copolymers, and can include branched functional groups along the side chain or at the ends of the side chains, creating different chemistries and architectures that can be linked together. The polydispersity of the side chains can further be used to create gradient brushes, with short side chains at one end leading to very long side chains at the other. As long as the chain can accept the polymer backbone unit at one end, and polymerization remains possible along that end group, the number of parameters that can be changed and tuned with these molecules creates a rich palette for synthesis, but also one that would be nearly impossible to simulate in toto. Thus, in this investigation, and in investigations to follow, researchers will primarily be limited to variation of a small number of parameters across a wide variety of studies in order to achieve even a partial understanding of the entire parameter space.

In this portion of the study, originally inspired by the work of Grubbs and coworkers[13], we focus on block bottle-brush copolymers in which each side chain is a simple linear chain of a single chemical species, and side chains of a given species are separated at opposite ends of the backbone, keeping in mind the target grafting density of one side chain per backbone unit (reflecting the macromonomer-based approach in Grubbs, et. al.); in the rest of this section, the two species simulated will be referred to as "type A" and "type B" monomers. In Grubbs' work, the degree of polymerization of the backbone varied from 100 to 400, generally centered on DPs of 100, 200 and 400; in this investigation, we have limited ourselves to 100-bead and 200-bead backbones in three basic configurations: 10-bead side chains on 200-bead backbones, 20-bead side chains on
100-bead backbones, and 20-bead side chains on 200-bead backbones (hereafter referred to as 10:200, 20:100, and 20:200, respectively). The restriction in the length of the side chains is based in part on the side chain degrees of polymerization in Grubbs’ work, which varied from roughly 20-60 depending on the specific system of interest), as well as a desire to retain backbone flexibility in bottle-brush molecules already restricted by the condition of tethering to the surface. We held constant the total simulation system size at roughly $1 \times 10^6$ total particles and defined the number of brush molecules and surface grafting density in order to arrive at an overall monomer density that represents a moderately dense layer. Bottle-brush layers are again tethered to a Lennard-Jones 9-3 wall similar to that used in Chapter 4 using non-interacting ”tether” beads either immobilized at the wall surface (“fixed” tethers; used to approximate covalent bonds to surface sites) or allowed to move laterally within the tethering plane but not out of it (“mobile” tethers; used to approximate physical bonds to the wall).

In a system with two basic bead types, there are six Lennard-Jones interaction parameters one must take into account: interaction energies $\epsilon_{AA}, \epsilon_{AB}$ and $\epsilon_{BB}$ describing the affinity (or lack thereof) between particle types and the particle sizes $\sigma_{AA}, \sigma_{AB}$ and $\sigma_{BB}$, which define the length scale of the simulation. In practice, however, it is often most useful to deal with particles that are assumed to be of the same size (i.e., $\sigma_{AA} = \sigma_{AB} = \sigma_{BB}$, and that the interactions between homopolymers of each type are similar (i.e., $\epsilon_{AA} = \epsilon_{BB}$). One case in which the last assumption may be violated is in systems where one component of the system condenses into a different physical form than the other under phase separation, such as in polymeric systems which phase-separate into hard and soft
domains[169]. In each of the simulations presented herein, we have used $\sigma_{AA} = \sigma_{AB} = \sigma_{BB} = \sigma = 1$ and $\epsilon_{AA} = \epsilon_{BB} = \epsilon = 1$, in Lennard-Jones units. Thus, the key parameter in two-component systems expected to phase-separate, as one might expect, is the heteromolecular interaction energy, $\epsilon_{AB}$.

In general, there are two ways to induce phase separation in bead-spring systems utilizing $\epsilon_{AB}$. In a bead-spring model like that used in Chapter 4, using the Weeks-Chandler-Andersen potential in which all interactions between particles are repulsive, one can tune the $\epsilon_{AB}$ parameter to make it A-B interactions unfavorable by increasing $\epsilon_{AB}$ relative to $\epsilon_{AA}$ and $\epsilon_{BB}$. In this form of the bead-spring model, where interactions are essentially about surmounting an energy barrier, this choice of $\epsilon_{AB}$ makes the barrier to A-B interactions that much more difficult to traverse. Such a model is much more computationally efficient, as it allows the same choice of $T = 1.0$ used in the previous simulations. In experiments, however, the complex nature of the relationship between solvent quality and temperature is important in the study of phase separation in block copolymer systems; even in such an implicit-solvent model, a lack of such a direct relationship between solvent and temperature makes this type of model computationally efficient but perhaps difficult to justify in comparison with reality.

The second method for inducing phase separation in bead-spring simulations is more analogous to experiment and also more often seen in the literature. In this formulation, the cutoff for the Lennard-Jones 12-6 potential is extended beyond the minimum at $r_c = 2^{1/6} \sigma$ to give interparticle interactions both repulsive and attractive components; common choices for an extended cutoff are $r_c = 2 \times 2^{1/6} \sigma$ and $r_c = 2.5 \sigma$. Including the attractive portion of the Lennard-Jones
potential in this way then drives phase separation through a decrease in the heterogeneous polymer interaction parameter $\epsilon_{AB}$ relative to $\epsilon_{AA}$ or $\epsilon_{BB}$, which has the effect of decreasing the attraction between A-B pairs relative to A-A or B-B pairs.

The extension of the cutoff to include attractive interactions also has the effect of making temperature an important parameter, as it now has the effect of modulating the relative strength of interparticle interactions and becomes a method of controlling the implicit solvent quality. Work by Grest and Murat\cite{170} on a model with cutoff $r_c = 2.5 \sigma$ determined the bead-spring theta temperature $T_\theta$, where excluded volume interactions are balanced by polymer-polymer attraction, to be $3.0 \pm 0.1 \frac{\epsilon}{k_B}$. Subsequent work has adjusted this estimate, giving $T_\theta$ as $3.18 \pm 0.02 \frac{\epsilon}{k_B}$\cite{171}.

In addition, however, the use of this extended Lennard-Jones interaction requires us to use a smaller time step, as the increase in the number of interactions based on the cutoff extension requires a higher frequency of sampling in order to accurately capture the more detailed interactions between particles. In WCA-based repulsive models, the time step can be extended to $0.01 \tau$ or more due to the efficiency of the model, the attractive/repulsive Lennard-Jones potential requires a time step commonly on the order of $0.005 \tau$, which is the time step used in these simulations. Simulations were monitored for equilibration via the side-chain and chain backbone radius of gyration, which was found to stabilize in roughly $75,000 \tau$; images presented in this section represent snapshots taken from the end of this equilibration process.

Thus, we have elected to use the model suggested by Grest and Murat, with Lennard-Jones cutoff extended to $2.5 \sigma$ and a simulation temperature of $2.0$
(using the same Langevin thermostat used in Chapter 4) to simulate a poor-solvent system that should encourage phase separation. As mentioned previously, the homopolymer interaction energy for the A and B polymer types have been set equal to unity; this is also the value of $\epsilon$ used for interactions between either side chain type and the backbone. The value of $\epsilon$ for A-B interactions must be lower than unity in order to drive phase separation. In the simulations shown in this phase of the investigation, the value of $\epsilon_{AB}$ was set to 0.5. This, along with the temperature providing an environment similar to a poor solvent, should provide a strong impetus to phase separation. Apart from the changes in simulation model explicitly mentioned here, all simulations were carried out in the same way as those in Chapter 4, with periodic boundary conditions in lateral directions and integration of the equations of motion via velocity-Verlet integrator in LAMMPS.

In a block-brush architecture with type A and type B monomers segregated at opposite ends of the backbone, the orientation of the bottle-brush becomes important. If all bottle-brushes in the simulation systems were oriented with type A side chains always tethered closest to the substrate and type B side chains always exposed to the free surface (termed "A-tethered" bottle-brushes in the remainder of this chapter; the converse is "B-tethered"), we would expect an equilibrated structure featuring an A-rich layer near the substrate with a B-rich layer on top. Such a system has its merits in investigations of fundamental polymer film structure: one could use this two-layer system to investigate the dependence of the interfacial width on the $\epsilon_{AB}$ interaction energy parameter, for instance. In an investigation of the morphological networks that can be created in polymeric systems where one end of the molecule is restricted to a surface site or surface
plane, however, the two-layer structure is essentially a result of an initial configuration in which the system is trapped. To attempt to avoid such a trapped result, we introduced an inversion parameter into the process of generating the initial configurations, defined as the probability with which the bottle-brush orientation was inverted from the default configuration of type-A side chains segregated at the tethered end of the bottle-brush. Setting this inversion parameter to 0.5, we expect to see systems in which roughly half the bottle-brushes are type A at the tethered end and half are type B at the tethered end.

5.2 Results and Discussion

The results presented in this section are primarily qualitative, consisting of visualizations of the target systems (using VMD[159]) intended to illustrate how changing just a few of the available parameters of brush structure and interaction can affect the adoption of complex morphologies. Quantitative analysis of the monomer type density and distribution of side-chain and backbone ends suggested that for initial configurations in which roughly equal numbers of type A-tethered and type B-tethered orientations are possible, monomers and chain ends became essentially evenly distributed throughout the bottle-brush layers, with small deviations (no trends noted) near the middle of the brush, where the two phases are confined by their presence on the same molecule to exist in proximity to one another.

In Figures 5.1 and 5.2, we examine top and bottom views of the central simulation system in which 10-bead side chains were grafted to 200-bead backbones with the backbone tethering sites fixed on the wall surface (in order to mimic
covalent bonding of bottle-brushes to the wall surface); no periodic images are included in these visualizations.

Figure 5.1: Top view of 20:100 simulation system after equilibration process. Polymer bonds and backbones have been suppressed in the image in order to portray separation of type A (white) and type B (blue) monomers.

Figure 5.2: Bottom view of 20:100 simulation system after equilibration process. Polymer bonds and backbones have been suppressed for clarity.

The bottom view of this system (Figure 5.2) gives the impression one would likely expect from a system of bottle-brushes immobilized at the base by fixed tethering points and a 50-50 distribution of A-tethered and B-tethered brushes; a rather fine-grained structure emerges that exhibits only local variation.
in type. The top view, on the other hand, exhibits a coarsening of features that suggests ready segregation between A-rich and B-rich regions. One might expect that this difference in upper and lower surfaces is the result of intrinsic backbone flexibility accommodating the coarser regions of separated side chains near the free surface while being limited near the wall, with subsequent side-chain flexibility allowing side chains near the free surface to move in order to segregate. In Figure 5.3, we can examine the average tension (bond force) along the backbone as a function of bond index (lower indices closer to the wall surface) in order to find out if significant force is building into the backbone as a result of stretching. With the exception of bonds within \( \approx 10^{-15} \sigma \), where higher tension suggests the effects of immobilization suggested before, and the region near the middle of the brush layer where a cusp in tension increase coincides with the transition from A blocks to B blocks (or vice versa), the lack of strong tension suggests that backbone flexibility within the brush and especially near the free surface contributes to the ability to form coarse phase-separated regions. The plot of monomer density vs. distance in Figure 5.3 suggests an interesting enrichment of type B monomers near the wall, which reverses at the mid-layer transition, and a build-up of type A monomers in the coarser mid-layer region and beyond, but is inconclusive aside from the suggestion that the extent of the bottle-brush layer (on the order of 55-60 \( \sigma \)) is significantly less than the initial backbone contour length, suggesting substantial flexibility in the brush backbones in collapsing into the layer seen.

In addition, in Figure 5.1, one may notice that the surface exhibits notable roughness; in some locations, specific A-rich or B-rich regions are separated by gaps where side chains and backbones, to the extent permitted by the latter,
Figure 5.3: Average bond force along the bottle-brush backbones (left) and density profile normal to the wall surface (right) for the 20:100 fixed-tether simulation at the end of the equilibration process. Error is on the order of symbol thickness.

separate almost entirely. This suggests both that the interaction energy parameter represents a strong tendency to phase separate between the A-type and B-type monomers, taking advantage of the flexibility of the backbones and side chains in the adoption of the phase-separated morphology: the much more favorable interactions between like side chains near the free surface causes those bottle-brushes to bend, with side chains possibly wrapping around backbones in order to separate more completely. The nature of the fixed tethers, however, ensures that bending can only occur locally, and significant gaps will form in regions of low density relative to the predominant species in those locations.

Because the top and bottom views cannot offer much in the way of impressions of the quality of the network within the phase-separated layer, we present in Figure 5.4 a series of snapshots in which cuts of width 20 $\sigma$ were made parallel to the y-z plane in order to show the interior of the layer.

The cuts through the interior of the bottle-brush layer help to indicate how the bottom structure changes as one progresses from the wall surface to the free surface. In a number of locations, one can see small islands with a structure
Figure 5.4: Snapshots of 20:100 fixed-tether bottle-brush final system morphology showing structure within the brush layer as a result of phase separation of type A (white) and type B (blue) side chains. Bottle-brush backbones have been suppressed to highlight side chains. Interval between slices is 20 $\sigma$.

consisting of type A monomers directly above type B monomers, or vice versa, suggesting that even as backbones bend to accommodate side-chain segregation in interfacial regions, local structure possibly prefers the initial configuration that causes the formation of these islands in the first place as a result of random inversion leaving some local clusters of similarly oriented bottle-brushes. At the boundary of these regions one finds vertical stripes of predominantly type A or type B monomers extending from the base of the brush to the free surface. In these regions, intrinsic backbone flexibility appears to allow bending that results in strong side chain phase separation. If we look at cuts from the top surface to the bottom (Figure 5.5), we get some indication of just how much the side chains have to reorganize in order to phase-separate.
Figure 5.5: Snapshots of 20:100 fixed-tether bottle-brush final system morphology showing interior structure. Bottle-brush backbones have been suppressed to highlight side chains. Interval between slices is 10 $\sigma$.

In the first three slices from the top down (Figure 5.5, top row), the structure seen on the top surface appears to be communicated well throughout. Gaps and furrows in the top surface are passed down to the lower levels of the brush, where we see that they arise primarily from regions dense in one type bounding a small island where the opposite orientation is seen. Beyond the third slice, however, the structure passes into the lower region of the brush where backbone stiffness is increased relative to the free surface and the structure becomes finer and finer until reaching the fixed structure present at the base of the bottle-brush layer. If we separate the structure into type A and type B components, we can visualize the network that forms as a result of the strong phase separation. This result for the 20:100 fixed-tether case is presented in Figures 5.6 and 5.7.

The first impression from each of these figures is that the strong separation of the two side chain types, coupled with the fixed tether sites, creates a disordered bicontinuous morphology that is relatively diffuse at the wall surface and broader and more ribbon-like toward the free surface. Separation between
the phases creates the large features seen near the top surface, which diffuse into smaller "feet" that help to tether the phases to the wall surface. The question of control of the feature size, from the diffuse structure seen near the wall to the large-scale ribbons near the top, is a question that may be answerable in future studies where parameters such as the interaction energy parameter $\epsilon_{AB}$ and the dimensions of the brush molecules can be treated in more depth. Nevertheless,
the possibility of such a gradient of feature size in a bicontinuous network may be promising for applications such as in bulk heterojunction solar cells, where control of such a stable network of two very different phases can help to combat charge recombination and conduct charges to the electrodes and where control over the width of proposed phase-separated structures is a necessity in increasing device efficiency.

If we change the type of tethering from a fixed site at the wall surface, reminiscent of a covalent tethering site, to a more physical tether, where the tethering group is allowed to move along the surface plane but not out of it, we get the morphologies seen in Figures 5.8 and 5.9.

Figure 5.8: Top view of 20:100 mobile-tether bottle-brush final system morphology, with individual bonds and backbones suppressed to highlight morphology.

The overall morphology seen from the top of the bottle-brush layer in Figure 5.8 bears a notable resemblance to the coarse features seen in the fixed-tether case in Figure 5.1, if not increased somewhat in the overall size of the regions created by the separate phases. In common with the fixed-tether case as well, we see that the penalty to mixing induced by the decreased interaction
parameter $\epsilon_{AB}$ leads to a roughness at the surface in the form of curved phase boundaries near the free surface of the brush layer as a result of type A and type B side chains strongly reorganizing to avoid the phase interfaces. What is notable in contrast to the morphology seen in the fixed-tether case is the structure of the bottom of the brush layer in Figure 5.9; whereas in Figure 5.2, the fine structure of the phase-separated regions reflected the lack of mobility of the chains near the tethering wall, in the case of mobile tethers it appears that the ability of the chains to move laterally along the surface has assisted in the coarsening of the two phases at both sides of the layer, with large portions of the bottom surface mirroring the top surface structure. In the fixed-tether case, side chains attempted to segregate as much as possible with the restriction of a constrained location at the wall forcing the backbones to bend. In the case of mobile tethers, however, local movement of entire brush molecules laterally along the surface can assist in avoiding any penalties to backbone bending and helps to create the larger features seen throughout the brush.
The regions of vertical coagulation of phases seen in the fixed-tether case appear to largely be limited to the phase boundaries in the mobile-tether case. The backbone tension and monomer density in Figure 5.10 are in line with this conclusion; again, we see a density that persists to 55-60 σ, suggesting backbone bending that allows brush collapse, as well as the same sort of alteration in density near the middle of the brush layer in the transition between blocks. The backbone tension, however, shows a reduction in linker tension of 25-30% and a faster decay to the low, constant tension seen throughout most of the rest of the brush (apart from the mid-brush transition, where a cusp is again seen). This reduction in tension in the backbone suggests that the mobile-tethered bottle-brushes are less constrained and face less stretching than their fixed-tether cousins, possibly due to mobility resulting in the adoption of more favorable contacts near the wall.

![Figure 5.10](image)

**Figure 5.10:** Average bond force along the bottle-brush backbones (left) and density profile normal to the wall surface (right) for the 20:100 mobile-tether simulation at the end of the equilibration process. Error is on the order of symbol thickness.

In Figures 5.11 and 5.12, the individual morphologies for the type A and type B monomers are again displayed. In this case, as discussed previously, the fine structure of the fixed-tether case, in which large-feature ribbons near the free surface give way to diffuse "foot" regions, is replaced by a much broader and
flatter set of morphologies that reflect the mobility of the bottle-brush molecules, as the larger flat regions suggest large spaces where molecules congregated based on their orientation relative to the surface. The mobility of the bottle-brush chains is clearly still predominantly local, as significant regions of orientation inversion can still clearly be seen, but one of the implications that may be taken from this part of the investigation is that physical tethering, where possible, may be able to take advantage of local chain mobility in these block bottle-brush copolymer layers to create large-feature bicontinuous networks whose size may be tuned by changing the structure and dimensions of the bottle-brush molecules themselves.

![Figure 5.11: Type A monomer network in 20:100 mobile-tether bottle-brush final system morphology. Bonds and backbones have been suppressed to highlight morphology.](image)

If we continue with the investigation of morphologies in simulations involving bottle-brush molecules physically tethered to the wall substrate (mobile tethers) and instead focus on short side chains (10 beads) and longer backbones (200 beads), we see the morphology depicted in Figure 5.13.

In this case, a glance at the top view in Figure 5.13 would at first suggest some form of striped morphology. Examination of the side view gives an indication
Figure 5.12: Type B monomer network in 20:100 mobile-tether bottle-brush final system morphology. Bonds and backbones have been suppressed to highlight morphology.

Figure 5.13: Top view (left) and side view (right) of 10:200 mobile-tether bottle-brush final system morphology. Bonds and backbones have been suppressed to highlight morphology. Periodicity has been included.

of exactly how these stripes are arranged. While in the previous mobile-tether case the mobility of the bottle-brush molecules appears to allow local rearrangement of A-tethered and B-tethered molecules into large groups with similar orientations, the impression from Figure 5.13 is that the mobility of bottle-brushes with shorter side chains and longer backbones can rearrange on larger length scales than that previous case. Here, instead of separating into regions based on islands of A-tethered or B-tethered bottle-brushes, the islands arrange into rows which appear
to run laterally, and then alternate between A-tethered and B-tethered groups as one moves in the lateral direction orthogonal to the axis of the rows. This forms long channels or cylindrical regions of A-rich and B-rich phases. To determine the structure of the phases when isolated, we look at the type A and type B morphologies, given in Figure 5.14.

![Figure 5.14: Side view of 10:200 mobile-tether bottle-brush final system morphology for type A monomers (left) and type B monomers (right). Bonds and backbones have been suppressed to highlight single-phase morphology.](image)

The morphologies in Figure 5.14 clearly show that the rows of A-rich and B-rich phases do not form isolated cylindrical regions, but actually serve to create what appears to be a bridged cylinder morphology in which the cylinders run parallel to the wall surface. This again produces two essentially continuous phases with similar structures that alternate spatially due to the confinement of side chains to individual bottle-brushes. The bottle-brushes themselves appear to have arranged in this structure again due to chain flexibility; in the bridge regions, at the interface between phases, we see backbone bending and side-chain rearrangement in order to accommodate the alternation between A-tethered and B-tethered bottle-brushes. Density and backbone tension calculations (Figure 5.15) again show similar characteristics to the 20:100 mobile-tether case: tension which decays quickly to a
near-constant value and features a cusp near the transition between blocks, and density which persists to \( \approx 55-60\% \) of the initial contour length of the backbones. In this 10:200 case, the density again shows an enrichment of one type relative to the other near the block transition, but otherwise suggests a much more even distribution of monomers between the two phases, possibly suggesting the apparent increase in order seen in the cylindrical structure.

Figure 5.15: Average bond force along the bottle-brush backbones (left) and density profile normal to the wall surface (right) for the 10:200 mobile-tether simulation at the end of the equilibration process. Error is on the order of symbol thickness.

A significant difference in both structure and morphology is obtained if we double the length of the side chains from the previous case, as seen in Figure 5.16.

In the case of 20-bead side chains and 200-bead backbones, the morphology that arises is cylinders oriented parallel to the bottle-brush backbones. The periodic boundary conditions in this case suggest a possible square packing of the cylinders, although the boundary conditions do not necessarily reflect the precise morphology one might expect, especially in cases with large features whose size is on the order of the simulation box dimensions. Nevertheless, the mobility of the bottle-brushes in this mobile-tethering case again suggest a longer-range pos-
sibility for aggregation, producing essentially two entirely separate phases, one of which aggregates into the cylinders and the other of which becomes the matrix between the cylinders. In this case, it is also clear from the morphologies and the density and backbone tension (Figure 5.17) that the chains are intrinsically stiff; backbone tension starts higher than in other cases and remains high throughout the brush, while density shows two extremely well-defined regions with density essentially inverted across the block transition, with the full density extending to nearly 90% of the initial contour length of the backbones.

One possible reason for the type A phase to form cylinders and type B phase to form the matrix may exist in the slight inequality in the type densities seen in Figure 5.17 resulting from the random orientation inversion. While the inversion process was designed, in this case, to keep the number of A-tethered and B-tethered brushes nearly the same, the randomness of the inversion was not restricted to create only 50-50 distributions; resulting small asymmetry produced a slight excess of A-tethered brushes, which may have caused the minority
Figure 5.17: Average bond force along the bottle-brush backbones (left) and density profile normal to the wall surface (right) for the 20:200 mobile-tether simulation at the end of the equilibration process. Error is on the order of symbol thickness.

B-tethered brushes to aggregate in the cylinders. This implies that we may add symmetry in the number of A-tethered and B-tethered bottle-brushes to the growing list of system parameters responsible for the morphologies that develop. The cylinder structure is mirrored between the top and bottom halves of the bottle-brush layer (see side view in Figure 5.16), and this mirroring is also evident in the density, where the density of A-type monomers below the block transition is almost the same as the B-type monomer density above the block transition. What appears clear, however, is that in this case, whether due to the extension of the bottle-brush backbones from the dense grafting of the side chains or some other effect, the bottle-brushes appear to prefer a highly extended conformation and possibly move along the surface as a rigid unit.

5.3 Conclusion and Future Outlook

The morphologies presented in this section of the simulation study are indicative of a fraction of the potential morphologies available as a result of the choices we made in which parameters to vary. From the strength of the polymer-
polymer interactions reflected in the chosen value of the interaction parameter, which presents a propensity for strong separation between the phases, to the choices of side-chain and backbone length, which reflect the intrinsic stiffness of the chains or lack thereof in bending and stretching to accommodate a given morphology, to the unexpected effects of a slight asymmetry in the populations of a given type of block brush in creating a cylindrical morphology, even the few parameters we have touched on in this study are sufficient to create a number of different structures. We have seen disordered bicontinuous networks that give way to highly structured and separate cylindrical domains resulting from only minor structural changes to a single block-brush architecture.

Research has shown that there is much more available to bottle-brush copolymers. Changing the number of blocks[8, 17], the structure of side chains[9, 10], the architecture of the side chains[15], the polydispersity (incidental or engineered) among the side chains and backbones, the distribution of the different side chain species along the backbone, etc. — all can potentially open the doors to a number of different effects in molecular self-assembly. The sheer magnitude of applications possible from these methods of self-assembly, from photoresists to bulk heterojunction devices, from biologically active surfaces to stimuli-responsive coatings, make us realize that our limitations are essentially the level of control that we can exercise in the laboratory to synthesize complex structures and our own ability to understand the complex relationships that bind so many parameters together.

These simulations are primarily intended to give a first indication of the rich palette of morphologies that may be possible with very modest variation in
the system parameters. As implied in the first part of this chapter, the parameter space from which multiblock morphologies can be drawn is massive in scope and altogether impossible to cover in a single study. Our hope is that this brief introduction to the parameter space will influence or excite further study of a systematic nature in order to aid in the development of predictive models for determining the true space of possible multiblock bottle-brush morphologies.
CHAPTER VI
CONCLUSION AND FUTURE WORK

In this work, we have attempted to show how computational simulation, specifically complementary molecular dynamics simulations at multiple time and length scales, can be used as tools for the evaluation of structure, order, orientation, and adsorption energetics at interfaces in systems requiring molecular-level or even atomic-level detail. We have done this in order to understand the formation and structure of interfaces and how we can effect large-scale or even macroscopic change by altering the size, shape, interactions or even the surface crowding between model small-molecule and polymeric systems and the surfaces onto which we deposit them. Nothing, of course, can replace experimental characterization of interfaces; it is from synthesis and characterization that computational simulation receives inspiration, and it is from accurate models based on experiment and synthesis that simulation derives its own accuracy and applicability. At interfaces, however, where direct evaluation of properties at nanometer and sub-nanometer length scales important to the evolution of interfacial structure becomes difficult or even impossible, simulation becomes an indispensable accompaniment and should only prove itself more and more useful as computational power and efficiency increases and as computational models gain both scope and resolution.

In Chapter 3, we started by suggesting all-atom molecular dynamics simulation as a way to obtain detailed information regarding the structure, orientation
and energies of adsorption for methane and chloromethane films on substrates of different structure, such as a flat featureless wall vs. a well-known and well-characterized molybdenum crystal surface, treated using different simulation models. The level of simulation highlighted the effects of both adsorbate and substrate geometry in the formation of surface layers: methane, with a symmetric structure preferred adsorption sites on the molybdenum surface above the unit cell centers, settling into interstitial sites more effectively than the asymmetric chloromethane, which could neither find a preferential adsorption nor a preferred molecular orientation, owing to its size and geometry. This portion of the study also discussed how differences in the models used for evaluation can have subtle effects on the structure and adsorption energy and thus highlights the need for accuracy in the simulation force fields for the accurate depiction of atomic level effects in the structure of adsorbed films.

In Chapters 4 and 5, we used a coarse-grained bead-spring model for molecular dynamics simulations to depict bottle-brush polymers at time and length scales more appropriate to macromolecules. In Chapter 4, this was used to investigate the structure within homopolymer bottle-brush molecules tethered to a surface to understand how the dimensions of the molecules and the surface grafting density could generate tension within the molecule as a result of excluded volume interactions, and how this tension causes structural rearrangements within the bottle-brush layers. Increases in surface grafting density were shown to first cause a lateral compression of side chains that quickly gives way to a forced reorientation of side chains to take advantage of the free surface available. Through this accumulation of tension and the structural rearrangements seen, specific surfaces
can be engineered by using the crowding to express different parts of the brush to the free surface, which should have applications in producing highly customizable selective interfaces utilizing side-chain structure to attract or repel specific compounds.

In Chapter 5, we then extended this homopolymer model to a two-component bead-spring simulation to suggest how bottle-brushes with multiple components, such as multiple side chain chemistries, can be modified in subtle ways to create a number of very different morphologies. Using block bottle-brush molecules tethered to a surface, we were able to show that even constrained bottle-brush molecules with disparate side chain chemistries will attempt to strongly separate in poor solvent to form morphologies ranging from small- to large-feature bicontinuous networks with little or no long-range ordering to highly ordered and structured cylindrical morphologies that can change orientation with a shift as simple as an increase in the degree of polymerization of the backbones or the inclusion of more and longer side chains. From the few parameters changed in this section and the enormous space of parameters available to change, it is clear that even the different morphologies seen in this section are not complete, as variation of other parameters is expected to elicit a number of other cooperative effects that can be used to tailor the phase-separated structures even further; this work represents the proverbial tip of the iceberg when it comes to the morphologies that can be envisioned.

In the future, we have envisioned extensions of these simulations and the ideas provided to study how the structure of bottle-brush tethered layers can be used to create a highly customizable polymer surface, akin to self-assembled mono-
layers or dense polymer brushes, that can be tailored based on application needs to create patterned surfaces of variable roughness such as the aforementioned selective-adsorption interfaces. Interest has already been shown in using bottle-brush layers for the selective adsorption of peptides and proteins from biosensors to coatings for biomedical implants; where peptide and protein adsorption presents a complex problem in basic adsorption, currently very little is known about even simple adsorption on bottle-brush tethered layers, or even how the inclusion of specific groups would affect the structure of the surface of such layers. We envision, then, a number of multi-scale simulations, either at the all-atom or subtly coarse-grained levels such as MARTINI, to investigate how the inclusion of specific chemical groups can be used to further modify the surface behavior of bottle-brush layers, especially regarding how the structure of side chains and the architectures available to the bottle-brush components can be tailored with specific groups in order to provide a versatile platform for either enhancing or rejecting adsorption.

Simulation will be of primary use in such investigations because of the large parameter space available to the construction of such bottle-brush surfaces and because of the synthetic complexity of creating such surfaces. One of the key benefits of computer simulation is in the ability to use \textit{in silico} methods to evaluate structure-property relationships in order to focus synthesis and characterization to specific systems of interest without going through the cost and effort necessary to evaluate all possible combinations of chemistry, structure, grafting density, etc., in the lab. In this way, we envision a long and fruitful collaboration between synthesis, characterization and simulation that should provide opportunities for years to come.
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