Effects of Molecular Architecture on the Structure and Dynamics of Supported Ultrathin Polymer Films

by

Amber Nicole Storey
Class of 2019
Faculty Advisor: Professor Francis W. Starr

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Abstract

Polymers are ubiquitous in our everyday lives and have uses in a wide range of industries, from electronics to food goods. Understanding properties of ultra-thin films has become a major interest in polymer science due to their use in semiconductors, adhesives, and artificial tissues. There has been a sustained interest in confinement since work by Keddie et al. (1994 EPL 27 59) published over 20 years ago suggesting the reduction in the glass transition temperature, \( T_g \), is due to the presence of a “liquid-like” layer at the air-polymer interface. Confinement effects result from a difference in the dynamics at the interfaces or the interference of a characteristic length scale; therefore, it is our aim to understand how confinement effects work in conjunction with complex polymer structures, which also affect dynamic properties like \( T_g \) and fragility. Dynamic fragility is key feature to know about polymer glasses for both their processing and application. However, there is still much debate on what polymer properties specifically contribute to the fragility. Much work has been done investigating this challenge using simulations, however prior studies have focused primarily on bead-spring type models instead of models that are more molecularly realistic. In this thesis, we employ molecular dynamics (MD) simulations of a coarse-grained polymer models that are chemically specific to polyethylene oxide (PEO) and polymethyl methacrylate (PMMA) with the aim to understand the role of molecular architecture on the structure and dynamics of bulk polymers and supported thin films. Our results show that when film thickness is reduced to 50 Å near \( T_g \), there are minor reductions in \( T_g \) for PEO and PMMA in-
indicating the dynamics are only weakly impacted by the differing molecular architecture. The structure, however, is highly affected due to the presence of the side group in PMMA. We also probe the film sensitivity to changes in the substrate interaction strength and observe that PMMA is more sensitive to changes of the substrate interaction strength because of the resulting disruption in monomer organization persisting nearly completely throughout the film.
Dedication

For two people, one who has just joined my life, my niece Aniala Danielle Morrison and another who has left, my late father Murray Storey. Both of you keep me going.
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Chapter 1

Introduction

The majority of people unknowingly interact with polymer glass via plastic, yet the idea that plastic is a glass seems far-fetched to those who have not studied it. It is usually much easier to think about and explain glass as a state of matter, just as with liquid and gas. A material is considered glass once the particles in the material exhibit solid-like behavior on cooling without molecules being arranged in a long-range lattice structure that is found in crystals. What induces this kinetic slowdown has puzzled scientists for the past century and is still of interest today. Our ancestors have been using natural glass (volcanic obsidian) since the stone age. However, we have learned from our prehistoric predecessors and now utilize a variety of glasses from synthetic glass that can be manufactured on a nanometer scale to high strength organic glass that can be used on buildings. There are numerous uses of polymers beyond the production of plastic and windows. Polymer-based materials are inexpensive to manufacture yet durable, making them ideal for many industrial applications. From solar cells [1] to the filling in a
1.1. POLYMERS AND THE GLASS TRANSITION

Despite the push towards more environmentally conscious consumerism, there has been a fast climb in the demand for polymer plastics over the past decade and the revenue for just the plastic production industry alone is expected to reach 654.38 billion USD by 2020 [3]. We have created a global need for polymer products that has never been seen before. The strong drive to use polymers in even more applications requires us to first take a step back and question what polymers are and what they can do. So what is a polymer?

A simple polymer is a large molecule consisting of $N$ repeat units called monomers. Polymeric materials are highly sought out not only because of the many properties they can take on, from viscoelasticity to electroconductivity[4], but also because they can be used to replace materials that are more costly to manufacture.

The polymers studied in this thesis, like most polymers due to their structural complexity, are glass-formers, meaning that as they are cooled they do not easily crystallize and instead form an amorphous solid. Macroscopically, amorphous solids behave like crystals, however microscopically they are nearly indistinguishable from liquids. Glass is not only the material of windows and bottles, but more broadly, a solid that is hard and rigid like a traditional solid but lacks the long-range order that appears in crystals. The simplest glass formation method is to cool a liquid past its melting point, avoiding crystallization, continuing into the supercooled regime, until the
material cannot statistically sample all configurations in the time allowed by the rate of cooling, thus becoming non-ergodic and falling out of equilibrium. This method of glass formation reveals one of the most intriguing features of the glass transition, a gradual change from one state to another. Unlike traditional phase transitions, for example, liquid to gas, the glass transition does not have a discontinuity in its thermodynamics. Therefore as temperature is decreased, the specific volume or enthalpy decreases continuously. The only indication of a transition is a shift in the rate of change from the liquid state compared to the glassy state, illustrated in Fig. 1.1. This shift appears as a characteristic “kink” in the curve where the system falls out of equilibrium. The temperature the material falls out of equilibrium is called the glass transition temperature, $T_g$. Although cooling is the simplest method to form a glass, it comes with its drawbacks. In the schematic Fig. 1.1, curve a and curve b represent the transition at different cooling rates, where curve a represents the faster rate. The different curves lead to different glass transition temperatures, meaning that this method results in a $T_g$ that is cooling rate dependent. This dependence arises because at slower rates the system is given more time sample configurations, rearranging into one that is a lower energy state. To combat this, the International Organization for Standardization (ISO) set in place experimental methods for differential scanning calorimetry (DSC) so that all calculations of $T_g$ were determined using the same temperature scan of 20 K/min [5].
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Figure 1.1: Temperature dependence of volume or enthalpy at constant pressure. A slower cooling rate represented by curve a results in the glass transition temperature $T_{ga}$. Depending on cooling rate, $b > a$, results in a cooling rate dependent $T_g, T_{gb} > T_{ga}$. This figure is reproduced from Ref. [6]

Mankind has been using and forming glass for over five millennia, however the mechanisms underlying the glass transition remains one of “the deepest and most interesting unsolved problems in solid state theory,” according to Nobel laureate, Philip W. Anderson [7]. There are two major schools of thought on glass transition: one is that glass is completely a dynamic phenomena and that glass is simply a liquid that flows at a rate too slow to access on a reasonable time scale, and the other is that the glass transition is truly a thermodynamic transition that exists at extremely long time scales. Putting these theoretically fundamental differences aside, there is still a qualitative understanding of the glass transition. The glass transition occurs when the
viscosity ($\eta$) or relaxation time ($\tau$) drastically increases over a small decrease in temperature and has become glass once $\eta = 10^{13}$ poise or $\tau = 100$s. Relaxation time is related to the inverse molecular mobility, therefore for large relaxation times, the molecular mobility is small. Relaxation time is further explained in Chapter 4. Despite being studied extensively [6, 8–11], there is still no unifying theory even within the two different schools of thought to describe the glass transition. Similar to the glass transition, it is poorly understood what microscopically causes materials to be fragile. Fragility is the slope steepness of the temperature variations in the structural relaxation. Large changes in relaxation time, $\tau$, as temperature varies indicates a fragile material. Fragility is a crucial glass characteristic for polymer processing because fragile materials become liquid-like with small changes in temperature. Depending on the application, it may be more advantageous to use particular polymers based on their fragility.
1.1. POLYMERS AND THE GLASS TRANSITION

Figure 1.2: Representation of various liquid’s viscosity as a function of $T_g$-scaled temperature, where $T_g$ is last tick mark on the $T_g/T$ axis. At low temperatures, fragile liquids exhibit a large change in steepness whereas strong liquids remain linear (Arrhenius). This figure is reproduced from Ref. [6]

Figure 1.2 displays the characteristic difference between ‘strong’ and ‘fragile’ glass formers. Even at low temperatures (relative to $T_g$), strong materials exhibit Arrhenius behavior which in terms of viscosity, $\eta$, is described by,

$$\eta = \eta_0 \exp \left[ \frac{\Delta F}{k_B T} \right], \quad (1.1)$$

where $k_B$ is the Boltzmann constant and $\Delta F$ is the change in activation free energy. The viscosity of ‘fragile’ liquids does not obey Eq. 1.1 rather, these liquids experience dramatic changes in viscosity approaching $T_g$. As a measure of how sensitive viscosity or relaxation time is to changes in temperature,
the rate of change at $T_g$ is known as the fragility index $m$,

$$m = \frac{\partial \ln \eta}{\partial T_{g}/T} \bigg|_{T=T_g}. \tag{1.2}$$

A similar equation is used to determine the fragility index from relaxation time where the $\eta$ is replaced with $\tau$, the structural (segmental) relaxation time. Although we have yet to gain a clear understanding of how the microscopic molecular structure of polymers affects their macroscopic properties, we do know that they do affect these macroscopic properties. It has been well understood that packing frustration significantly affects fragility and the glass transition temperature.

The goal of our study is to understand how polymers with structural differences affects fragility with a focus on the existence of side groups versus no side groups. However, there are several defining properties of polymers such as molecular weight (chain length), backbone flexibility, and side group bulkiness and flexibility. PEO has a flexible backbone and no side groups while PMMA has a stiff backbone and flexible side groups making them ideal candidates of our study [12]. It has been well studied how other structural differences like backbone rigidity, affects dynamics [13–15]. However, there is much more to uncover regarding how structural differences, other than how backbone rigidity, affects dynamics within films.
1.2 Polymer Films

The push towards nanofabrication has caused the study of polymer thin films to be of enormous importance not only to academics but also for industry. The dynamic behavior of polymer in bulk often does not agree with the dynamics within thin films, especially in films under 50 nm. However, the cause of this divergent behavior has yet to be explained by a single experimentally verified theory. The challenge of understanding polymer film’s thickness dependence has become one of the main foci of modern polymer physics [16].

Two widely studied types of polymer films are free-standing and supported. Free-standing films have no confining boundaries making them unstable above $T_g$; as such, the creation of free-standing films requires a non-equilibrium process below $T_g$, making their behavior rather sensitive to the details of preparation. Supported films, which are the focus of this work, are supported on one interface with a substrate and the other surface is a free air interface. These films can be readily made by the gradual cooling of a fluid film until it vitrifies at $T_g$. Many experimental [17–21] and computational [22, 23] studies have shown that there is a dramatic shift in properties like $T_g$ and mobility for polymers under confinement when compared to properties in bulk.
Figure 1.3: The reduction of $T_g$ for polystyrene films supported on a neutral silicon substrate studied at three different molecular weights ($M_w$). Note that there is little variation in the depression of $T_g$ with a change in $M_w$, which is represented by the three different symbols. This figure is reproduced from Ref. [17]

It is strongly suggested that for most materials, motion near the free surface (polymer-air interface) is much faster than motion in bulk. There is a suggested enhanced mobility at the free surface that causes a reduction of $T_g$. However, at the polymer-substrate interface, $T_g$ can shift in either direction depending on the polymer-substrate interaction strength which can be seen in Fig. 1.4. Therefore, the $T_g$ of the entire film is dependent on the effects at the two interfaces. The highly mobile layer at the polymer-air interface creates a liquid-like region in the film altering the dynamics. As film thickness decreases the interfacial effects carry heavier importance for the overall film dynamics. However, the reported shifts in $T_g$ for many polymers depends on technique which is questioned in Ref. [24]. The results of different methods
are swayed by using either the thermodynamic or dynamic definition of $T_g$ which are highly influenced by different regions of the film. For our study, we will make all comparison of $T_g$ using the same method to avoid the film region bias that arises from using different definitions of $T_g$.

Figure 1.4: The relaxation time of 10 simulated supported polymer film systems with varying substrate-polymer interaction strengths, $\epsilon_{sp} = 0.1, 0.25, 0.5, 0.75, 1.0, 1.25, 1.5, 2.0, 2.5, \text{and} 3.0$ as a function of distance from the substrate. The values of $\epsilon_{ps}$ are given in as fractions of the polymer-polymer interaction strength. This figure is reproduced from Ref. [24]

In Ref. [24] the dependence of the segmental relaxation time $\tau_\alpha$ on $\epsilon_{ps}$, which is the interaction strength between the substrate and polymer film, is made clear. Since the glass transition temperature, $T_g$, can be extrapolated from the relaxation time if there is an enhancement or reduction in relaxation time the same shift can be seen in the glass transition temperature. There are
drastic changes in $\tau_\alpha$ near the substrate. For weakly interacting substrates there is a downward shift in the relaxation time. As the $\epsilon_{ps}$ increases above $\epsilon_{ps} = 0.75$, represented by the blue curve in Fig. 1.4, so does the shift in $\tau_\alpha$. Below $\epsilon_{pp} = 0.75$, there is a reduction in $\tau_\alpha$ since this is the crossover from a neutral to a repulsive substrate. The $\alpha$ subscript on $\tau_\alpha$ designates the type of relaxation. $\alpha$-Relaxation is associated with the motion that arises from particles becoming freed from their surrounding neighbors that were preventing the motion previously, similar to becoming freed from a cage. Caging is a phenomenon of glass systems that largely contributes to the confounding nature of glass formation. Upon cooling, the motion of individual particles is constrained because of the dramatic kinetic slowdown glass formers experience. As neighboring particles slow down, that forces the motion of individual particles to slow down as well and in turn slows the motion of its neighbors. This creates an effective cage, only allowing local vibrational motion. For particles to move on a larger scale, they typically move in some collective fashion. The reliance of a particle’s motion on its neighbors is called cooperative motion. $\alpha$-Relaxation is when the large-scale motion of “breaking the cage” ceases, which is the motion that dominates glass dynamics. This is why many studies focus solely on $\alpha$-relaxation which from this point will be referred to as relaxation or segmental relaxation since this thesis does not focus on any other type of relaxation.
1.3 Effect of Molecular Structure on Glass Formation

With advancements in modeling capabilities and experimental methods, understanding the role of chemical composition and architectures in glass formation has come to the forefront of polymer science. However, there has yet to be a consensus on how different molecular features shift $T_g$ in confinement. The variation of $T_g$ can be linked to confinement, packing frustrations, collective motion and many more effects; therefore, it is challenging to pin down these shifts to one cause. By having a focus on particular properties, there is some hope to understand how the molecular features affect glass formation.
There are major categories of molecular properties that are of particular interest:

- chain/backbone stiffness [13, 14, 26, 27]
- presence of side groups
  - side group size [28]
  - side group length [29]
  - side group stiffness [27, 30]

From the literature, we know that higher backbone and side group stiffness leads to higher packing frustrations. These packing frustrations lead to an enhancement in $T_g$. However, many complex polymers have several of these properties, complicating a prediction of the structural effects on the overall dynamics. Work by Dudowicz et al. [29] and Kunal et al. [12] shows that when comparing polymers that have side groups, the most important factor is the stiffness of the side group relative to the stiffness of the backbone followed by the size of side groups.
1.4. CONTRIBUTIONS OF THIS THESIS

However, the impact that the size of side groups has on dynamics and $T_g$ is not so trivial. For thin films, as the size of side groups increases, there is a large reduction in $T_g$ near the free surface but an enhancement near the substrate. There is still much to be explored in order to quantify the effects of molecular structure on dynamics, especially in confinement.

1.4 Contributions of this Thesis

In this thesis, we focus on computational molecular modeling to quantify the structural and dynamical differences between polymers with distinct molecular structures. Even further, we want to understand how these differences
are affected by nanoconfinement. The following outlines the contributions of this thesis:

- There is a significant difference in the arrangement and organization of the polymers in films. The enthalpic drive for the side groups of PMMA to align with the substrate causes a small layer of side group beads to buffer the substrate from the rest of the chains. Also, the density profile of the thin films indicates that PEO packs more efficiently near the substrate because there is less packing frustration for PEO since it lacks the side groups that are present in PMMA.

- Despite the difference in packing near the substrate and unique molecular structures of PEO and PMMA, the dynamics are only weakly impacted. Looking at the dynamics in three different regions of the film (near the substrate, near the free interface, and in the interior), we can see that the reduction in relaxation time caused by the free surface is effectively canceled out by the enhancement in relaxation time caused by the substrate layer in both PEO and PMMA. The interior of the films behaves bulk-like resulting in the dynamics of the overall film to be similar to the bulk. By investigating the three regions of the film we do notice however that PMMA film a higher sensitivity to the substrate which is reflected in the $D$ parameter from the VFT equation.

- We also investigate the impact that the interaction strength between the polymer and substrate, $\epsilon_{ps}$, has on the dynamics within the film. We observed that when $\epsilon_{ps}$ is enhanced, the PMMA system experiences
large disruptions in monomer organization compared to the neutral interaction system. The consequences of the monomer disorganization of the PMMA film is seen in the relaxation profile where the substrate interfacial effects are observed farther away from the substrate interface than in the neutral system. This fact in conjunction with the fact that we were unable to equilibrate the substrate layer for low temperatures lead us to conclude that PMMA is more sensitive to the substrate than PEO due to the side group and rigid backbone.

Understanding how molecular architecture affects the structure and dynamics in ultrathin films enables us to further the use of polymers in applications. Having a fine control over film properties is invaluable for applications like medical devices where polymers are implemented for bone grafting and polymer solar cells where film properties affect efficiency. This thesis motivates future work to investigate the effect of molecular architecture on dynamics with more control over molecular properties, instead of staying true to the properties of a real polymer. This way we are able to understand how individual properties affect the film.
Chapter 2

Computational Simulation and Modeling

Computer simulations have allowed us to study properties that are not readily accessible experimentally [31]. Molecular simulations have substantially improved the field of polymer science by allowing theorists and experimentalist to probe molecular scale structure and dynamics that cannot be readily probed experimentally. Computational methods give us the ability to calculate many-body systems with expansive time and length scales. Given that there is yet to be an analytical solution to the many-body problem, using computational methods to find numerical solutions is the closest we can get.

There are two main techniques of molecular simulation, Monte Carlo (MC) and molecular dynamics (MD). These computational methods complement experiment by giving experimentalists a view of the microscopic ongoings to some macroscopic phenomena. Using MD or MC is a matter of what system is being studied. For example, MC simulations are commonly used
for gas or low density systems because it allows for more efficient energy barrier crossings [32]. However, for more dense systems MD simulations are preferable and unlike MC, MD keeps a measure of time allowing dynamical analysis. This work is concerned with how each system of interest behaves dynamically, thus an MD approach was used. Although MD simulations are computationally demanding in their attempt to mimic nature, it is of the utmost importance to use them to get a grasp of the dynamics of complex materials.

\section*{2.1 Simulation Details}

In this section, the simulation model and preparation for both the polymer melt and film systems is described. All simulations were performed using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [33] molecular dynamics package. The program VMD was used to produce visualizations of the molecular systems [34]. Coarse-grained (CG) representations of PEO [35] and PMMA [36] were used to model supported ultrathin films opposed to an atomistic approach. Coarse-graining reduces the total number of particles need to model a polymer by grouping certain atoms together into a coarse site which is illustrated in Fig. 2.1. Although, all-atom molecular modeling explicitly represents each atom in the system and are more chemically accurate, modeling each atom in the system is more computationally expensive, thus a coarse-grained approach is preferable.
Figure 2.1: On the left is the all-atom depiction of a polymer where hydrogen is orange, oxygen is pink and carbon is blue. On the right the same polymer that has been coarse-grained by grouping the carbon-oxygen-carbon sequence together along with the two hydrogens bonded to the oxygen into one green bead. The number of particles required for simulations significantly decreases going from an all-atom model to a coarse-grained model.

Periodic boundary conditions are used in all simulations to reduce boundary effects and create an effectively infinite simulation size while only needing a fraction of the particles necessary to have a statistically meaningful simulation.

2.1.1 PEO

Polyethylene oxide (PEO) has several medical and biological uses, primarily used as a basis for laxatives. PEO is also commercially used as a lubricant for razors and printer heads. The selection of PEO for this study is based on its simple molecular structure. It has a relatively flexible backbone and no side groups making it an ideal candidate for a study on the impact of
molecular structure. The chemical formula of PEO is \( \text{H-}(\text{O-CH}_2\text{-CH}_2)_n\text{-OH} \).

Figure 2.2: The gray circle overlays the atoms that are included in each coarse-grain site for PEO model.

We have coarse-grained PEO by making every C-O-C sequence a bead illustrated in Figures 2.2 and 2.3. The end bead, although not a C-O-C sequence, was coarse-grained in the same manner as the repeat units. Each bead weighs 44 g/mol.

Figure 2.3: The gray circle overlays the atoms that are included in each Coarse-Grain site for PEO model. For this visualization of the PEO chain, hydrogen is orange, oxygen is pink and carbon is blue. For illustrative purposes, a shorter chain length was used for this visualization.

The Lennard-Jones (LJ) potential was applied for interactions between non-bonded monomers, meaning any two monomers not connected via a bond, defined as,

\[
V_{\text{non-bonded}}(r) = V_{\text{LJ}}(r) + S(r),
\]

where \( S(r) \) is a function that shifts the potential smoothly to zero between the designated cutoffs, \( r_1 = 9.0\text{Å} \) and \( r_c = 12.0\text{Å} \). These cutoffs are used to
2.1. SIMULATION DETAILS

designate when the function $S(r)$ should start (at $r_1$) and stop (at $r_c$) the shifting, where the potential at $r_c$ should be zero. $V_{LJ}$ is defined as,

$$V_{LJ}(r) = 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r} \right)^{12} - \left( \frac{\sigma_{ij}}{r} \right)^{6} \right], \quad (2.2)$$

where $\sigma$ is the minimum distance between monomers, roughly the monomer diameter and $\epsilon$ is the well depth at the minimum of the potential. These parameters are set to $\sigma = 4.3 \text{Å}$ and $\epsilon = 0.8066 \text{Kcal/mol}$ for the interaction between two PEO monomers. The indices $ij$ distinguish polymer-polymer (pp), polymer-substrate (ps) and substrate-substrate (ss). It should be noted that nearest neighbors do not interact via the LJ potential for PEO. Bonded particles, meaning nearest neighbors that are connected via a bond, are bonded by harmonic bonds with the potential

$$V_{\text{bond}} = K_b(b - b_0)^2, \quad (2.3)$$

where the bond force constant is $K_b = 20.32 \text{Kcal/mol} \cdot \text{Å}^2$ and the equilibrium bond length is $b_0 = 3.30 \text{Å}$. There is also a defined angle potential,

$$V_{\text{angle}} = K\left[\cos(\theta) - \cos(\theta_0)\right]^2 \quad (2.4)$$

similar to the bond potential constants, $K = 10.16 \text{Kcal/mol}$ is an angle constant and $\theta_0 = 130^\circ$ is the equilibrium angle between monomers. The
2.1. SIMULATION DETAILS

dihedral potential is defined by,

\[ V_{\text{dihedral}}(\phi) = \sum_{i=1}^{m} K_i (1 + \cos(n_i\phi - d_i)), \]

where \( m = 4 \), so there are four \( K, n \) and \( d \) values which are listed in Table 2.1.

\begin{center}
\begin{tabular}{c|ccc}
\hline
\( i \) & \( K \) (Kcal/mol) & \( n \) & \( d \) (\(^\circ\)) \\
\hline
1 & 0.46845 & 1 & 180 \\
2 & 0.04302 & 2 & 0 \\
3 & 0.07887 & 3 & 0 \\
4 & 0.02868 & 4 & 0 \\
\hline
\end{tabular}
\end{center}

Table 2.1: Dihedral potential parameters for \( K, n, \) and \( d \) from Eq. 2.5

Ref. [35] has more details on the potentials used in this model.

2.1.2 PMMA

Contrasting the simple structure of PEO, PMMA is more architecturally complex. A 2-beads-per-monomer coarse-graining method was used for PMMA. By coarse-graining backbone atoms into one bead and the side group atoms into another, this model allows us to track the motion of the backbone and side group separately. By modeling these separately, we are able to see the effect of the backbone and the side group independently on the overall dynamics and structure in the film. The chemical formula for PMMA is \((C_5O_2H_8)_n\). Fig. 2.4 clarifies how the backbone chemical structure was coarse-grained separately from the side group.
2.1. SIMULATION DETAILS

Figure 2.4: This graphic shows the atoms that are included in each coarse-grained bead. In gray is the backbone bead which groups the atoms of the methacrylate backbone and the methyl side group in yellow.

The backbone bead (referred to as A, in gray) has mass 85.1 g/mol and the side group bead (referred to as B, in yellow) has mass 15 g/mol.

Figure 2.5: The gray shadows represent backbone beads and the yellow shadows are the side group beads.
2.1. SIMULATION DETAILS

The non-bonded beads interact with the same shifted LJ potential as Eq. 2.1, where the potential is shifted to have a smooth cutoff between \( r_1 = 12.0 \text{Å} \) and \( r_c = 15.0 \text{Å} \). For the LJ potential, Eq. 2.2, there are six defined parameters: \( \epsilon_{AA}, \epsilon_{BB}, \epsilon_{AB}, \sigma_{AA}, \sigma_{BB} \) and \( \sigma_{AB} \), where A represents the backbone bead and B is the side group bead.

Table 2.2: Parameters of Lennard-Jones Potential for PMMA

<table>
<thead>
<tr>
<th>Bead</th>
<th>( \epsilon_{ij} ) (Kcal/mol)</th>
<th>( \sigma_{ij} ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA</td>
<td>0.5</td>
<td>5.5</td>
</tr>
<tr>
<td>BB</td>
<td>1.5</td>
<td>4.42</td>
</tr>
<tr>
<td>AB</td>
<td>0.866</td>
<td>4.96</td>
</tr>
</tbody>
</table>

The bonded particles interact via the same harmonic bond as PEO (Eq. 2.3), with spring constants \( K_{b,AA} = 105.0 \text{ Kcal/mol·Å}^2 \), \( K_{b,AB} = 39.86 \text{ Kcal/mol·Å}^2 \) and bond lengths \( b_{0,AA} = 2.735 \text{ Å} \) and \( b_{0,AB} = 3.658 \text{ Å} \).

The angle potential has two different forms, one for the AAA-angle and another for the AAB-angle. The AAA-angle potential is,

\[
V_{\text{angle,AAA}}(\theta) = -k_2 T \ln \left[ a_1 \exp \left( -\frac{\theta - \theta_1}{b_1} \right)^2 + a_2 \exp \left( -\frac{\theta - \theta_2}{b_2} \right)^2 \right], \quad (2.6)
\]

where \( a_1 = 2.294 \times 10^{-2}, b_1 = 9.493^\circ, \theta_1 = 121.0^\circ, a_2 = 4.367 \times 10^{-3}, b_2 = 6.210^\circ, \) and \( \theta_2 = 158.5^\circ \). The AAB-angle potential is,

\[
V_{\text{angle,AAB}}(\theta) = k_2 (\theta - \theta_0)^2 + k_3 (\theta - \theta_0)^3 + k_4 (\theta - \theta_0)^4, \quad (2.7)
\]

where \( \theta_0 = 96.85^\circ \), \( k_2 = 9.881 \text{ Kcal/mol·rad}^2 \), \( k_3 = -15.12 \text{ Kcal/mol·rad}^3 \), and \( k_4 = 6.589 \text{ Kcal/mol·rad}^4 \).
Similarly, the dihedral angle must be separated into two forms, one for the BAAB dihedral and another for the AAAA dihedral. The form of the AAAA dihedral is,

\[ V_{\text{dihedral,AAAA}}(\phi) = \sum_{k=1}^{5} A_k \cos^{k-1}(\phi), \]  

(2.8)

where the parameters \( A_1 - A_5 \) are the following:

<table>
<thead>
<tr>
<th>AAAA Dihedral Parameters (Kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_1 )</td>
</tr>
<tr>
<td>4.380</td>
</tr>
</tbody>
</table>

Table 2.3: Parameters for PMMA AAAA Dihedral Potential

The BAAB dihedral angle potential has the same form as the AAAA potential with different coefficients,

<table>
<thead>
<tr>
<th>BAAB Dihedral Parameters (Kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_1 )</td>
</tr>
<tr>
<td>4.519</td>
</tr>
</tbody>
</table>

Table 2.4: Parameters for PMMA BAAB Dihedral Potential

This model was developed by Hsu et al. and for more detail on how this model was parameterized refer to Ref. [36].

2.1.3 Substrate

A substrate is used in film systems to support the polymer melt. To keep the substrate from becoming integrated within the film, the substrate partii-
icles are tethered to a fixed wall on the bottom of the simulation box. The substrate is the (111) face of an FCC silicon lattice.

![Figure 2.6: Representation of substrate used in all film simulations on the left. The image on the right illustrates the position of the substrate used for supported films. The blue beads represent the polymer monomers.](image)

The particles are allowed to be locally displaced using a spring with spring constant \( k = 16.667 \text{ Kcal mol}^{-1}\text{Å}^{-2} \), keeping the particles near their equilibrium position. The interaction distance \( (\sigma) \) obeys the Lorentz rule:

\[
\sigma_{ps} = \frac{\sigma_{ss} + \sigma_{pp}}{2},
\]

(2.9)

which is an arithmetic mean. The interaction strength between the polymer beads and the substrate was calculated by relating the components of the surface tension and the work of adhesion for the materials composing the
2.2 Simulation Procedures

A critical aspect of doing any analysis of MD simulations is to ensure the system is well equilibrated. By using unentangled polymer chains, we can avoid entanglement dynamics and reach equilibrium in a more accessible time scale [39]. The entanglement molecular weight for PEO is 2000 g/mol which is roughly 45 beads [40]. The preferred entanglement weight of PMMA is 11800 g/mol which is about 118 monomers, where each monomer has one substrate and polymer film.

\[
\frac{\epsilon_{sp}}{\epsilon_{pp}} = \frac{\sqrt{\gamma_{sub}^d \gamma_{poly}^d} + \sqrt{\gamma_{sub}^p \gamma_{poly}^p}}{\gamma_{poly}}
\]

(2.10)

where the surface tension is \(\gamma = \gamma^d + \gamma^p\) [37, 38]. The superscripts \(d\) and \(p\) refer to the dispersion and polar components of surface tension, respectively. The subscripts \(sub\) and \(poly\) refer to the substrate and polymer, respectively. We used experimental values for surface tension to have realistic interactions between the film and the substrate. From these parameters, the calculated \(\epsilon_{ps}\) and \(\sigma_{ps}\) for PEO and PMMA were:

Table 2.5: Lennard-Jones Parameters for Polymer-Substrate Interaction

<table>
<thead>
<tr>
<th>System</th>
<th>Bead</th>
<th>(\epsilon) (Kcal/mol)</th>
<th>(\sigma) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO</td>
<td></td>
<td>0.9806</td>
<td>3.41</td>
</tr>
<tr>
<td>PMMA</td>
<td>sA</td>
<td>0.4623</td>
<td>4.45</td>
</tr>
<tr>
<td></td>
<td>sB</td>
<td>1.387</td>
<td>3.915</td>
</tr>
</tbody>
</table>
backbone bead and one side group bead [41]. Therefore, the chain lengths 20 beads per chain for PEO and 100 beads per chain (50 monomers) for PMMA were optimal for avoiding entanglement.

### 2.2.1 Bulk System Preparation

Periodic boundary conditions are applied in the $x$, $y$, and $z$ directions. PEO and PMMA systems are initialized with the system density at $1.0 \text{ g/cm}^3$, where system size is $N = 6000$ CG atoms for PEO and $N = 10000$ CG atoms for PMMA (5000 backbone CG atoms and 5000 side group CG atoms). The system is equilibrated at a high temperature in the NVT (fixed number of particles, volume and temperature) ensemble for 1 ns using an integration time step of $\Delta t = 1 \text{ fs}$, then cooled down to a given temperature at the rate $0.001 \text{ K/s}$. At this stage, we set the box size to fluctuate by changing to an NPT (fixed number of particles, pressure and temperature) ensemble, at pressure $P = 0 \text{ atm}$. By allowing this system to run for 1 ns at fixed temperature and pressure, we ensure that we can get a statistically meaningful average box size for the system which is calculated from the thermodynamic volume output every 1000 time steps. With this new box size calculated from the volume of the system at $P=0 \text{ atm}$, we can run the simulations in the NVT ensemble with essentially zero pressure. We want to conduct all production run simulations in the NVT ensemble because it is the ensemble used to conduct experiments. The system is run at NVT for another 1 ns before data collection begins.
2.2. SIMULATION PROCEDURES

2.2.2 Film System Preparation

The polymer section of the film is prepared similarly to the bulk system, where the integration time step of all simulations is $\Delta t = 1$ fs and the system undergoes several annealing cycles to equilibrate the film. To create a film with height $50\,\text{Å}$ at $T_g$, PEO films have system size $N = 3000$ CG atoms and PMMA has system size $N = 5000$ CG atoms, excluding the substrate particles. Since the (111) face of the FCC lattice is triangular the substrate cannot be made square. Therefore we create a substrate that is roughly square with side lengths $20\sigma$ for PMMA and $15\sigma$ for PEO. To model a thin film we have applied periodic boundary conditions in the $x, y$-directions, parallel to the substrate, with the $z$ dimension left non-periodic to model a free surface on top of the film creating an effective pressure of $P = 0$ atm. All film simulations are conducted at fixed NVT to keep the periodicity of the substrate lattice. The system is equilibrated for 1 ns with purely repulsive walls at the top and bottom of the simulation box in the $z$ direction. The interaction between the applied walls and the substrate is a 9-3 Lennard-Jones potential. These walls are implemented during the first cycle of equilibration to ensure the polymers do not travel towards the top of the simulation box and no beads penetrate or deform the substrate once substrate CG beads are introduced. In the next cycle of equilibration, the substrate is inserted into the simulation box. Since the substrate and polymer beads have a slight attraction, similar to the polymer-polymer attraction, this allows any gap between the film and the substrate to be bridged and for the film to sit naturally on the substrate. The system is then equilibrated again for 1 ns at the
desired temperature before the production runs begin.
Chapter 3

Impact of Molecular Architecture on Structure

It still remains unclear how molecular attributes of polymers contribute to the glass transition. Jamming and packing have historically been linked to the glass transition therefore, it is important to understand the structure and organization of monomers and polymer chains in confinement. In this chapter, I will discuss the observed structural and organizational differences of the PEO and PMMA films.

3.1 Pair Correlation Function $g(r)$

The pair correlation function, $g(r)$ or the radial distribution function, is an important static property that quantifies the local structure. $g(r)$ can also be used to define thermodynamic averages such as energy, $\langle U \rangle$, and pressure $p$ [42]. The pair correlation function can be obtained from the relationship
with the van Hove function, \( G(r, t) \). The van Hove function is defined as,

\[
G(r, t) = \frac{1}{N} \left\langle \sum_{i=1}^{N} \sum_{j=1}^{N} \delta(r - \mathbf{r}_i(t) + \mathbf{r}_j(0)) \right\rangle
\]

\[
= \frac{1}{N} \left\langle \sum_{i=1}^{N} \delta(r - \mathbf{r}_i(t) + \mathbf{r}_i(0)) \right\rangle + \frac{1}{N} \left\langle \sum_{i\neq j}^{N} \delta(r - \mathbf{r}_i(t) + \mathbf{r}_j(0)) \right\rangle
\]

\[
G(r, 0) = \delta(r) + \frac{1}{N} \left\langle \sum_{i\neq j}^{N} \delta(r - \mathbf{r}_i(0) + \mathbf{r}_j(0)) \right\rangle
\]

\[
G(r, 0) = \delta(r) + \rho g(r)
\]

(3.1)

where \( \delta(\cdot) \) the three-dimensional Dirac delta function, \( \rho \) is the number density, \( N/V \), and \( \mathbf{r}_i \) and \( \mathbf{r}_j \) are the vector positions of particles \( i \) and \( j \). We have defined the function \( g(r) \) as,

\[
g(r) = \frac{1}{\rho N} \left\langle \sum_{i\neq j}^{N} \delta(r - \mathbf{r}_i(0) + \mathbf{r}_j(0)) \right\rangle
\]

(3.2)

Since our system is isotropic, \( g(r) \) only depends on \( r = |r| \) and we can simplify Eq. 3.2 by dividing by the phase space factor, \( 4\pi r^2 \). This simplification results in the static pair correlation function \( g(r) \),

\[
g(r) = \frac{1}{4\pi r^2 \rho N} \left\langle \sum_{i\neq j}^{N} \delta(r - |\mathbf{r}_i(0) - \mathbf{r}_j(0)|) \right\rangle
\]

\[
= \frac{\langle n(r) \rangle}{4\pi r^2 \rho \Delta r}
\]

(3.3)

where \( \langle n(r) \rangle \) is the average number of particles within a separation \( r \) and \( r + \Delta r \), where \( \Delta r = 0.1 \) [43].
3.1. PAIR CORRELATION FUNCTION $G(R)$

Figure 3.1: The pair correlation function, $g(r)$, of bulk PEO and PMMA where $r$ is the distance between a pair of atoms, measured in Å. The labeled peaks of interest for PMMA (in red) are a) the backbone-backbone bond length, b) is the backbone-side group bond length, c) is the backbone-side group pair interaction length and d) is the backbone-backbone pair interaction length. For PEO, the peak e) is from the bonded interactions and f) is from the pair interactions.

For the purposes of Fig. 3.1, $g(r)$ was calculated at a relatively low temperature, $T/T_g = 1.11$ to result in sharper peaks. At high temperature, the increased thermal energy allows monomers to easily displace from their equilibrium positions producing weaker peaks of $g(r)$. 
3.1. PAIR CORRELATION FUNCTION $G(R)$

Figure 3.2: $g(r)$ of (a) PMMA and (b) PEO evaluated at different temperatures. The curves have been shifted and separated by 1 to clarify curve features. We see that the peak location are the same for all temperatures however the features become sharper as temperature is decreased.

The radial distribution function allows us to quantify the distinct molecular structures of PEO and PMMA such as the pair interaction length and the bond length between the different monomers. From $g(r)$, we can see that
3.1. PAIR CORRELATION FUNCTION $G(R)$

PEO has longer bonds than the backbone-backbone bond of PMMA and very similar pair interaction lengths.

3.1.1 Structure Factor $S(q)$

While the radial distribution function is straightforward to compute for simulations, it is only indirectly measured experimentally. Therefore, looking at the structure factor, $S(q)$, which can be directly measured from scattering experiments such as, X-ray or neutron diffraction Since $S(q)$ is a Fourier transform of $g(r)$, it more plainly reflects periodicities in the intramolecular packing. As such, $S(q)$ is particularly helpful to assess the degree of crystallization. The structure factor is defined as:

$$S(q) = \frac{1}{N} \langle \rho(q)\rho^*(q) \rangle, \quad (3.4)$$

where $q$ is a wave vector and $\rho(q) = \sum_{j=1}^{N} e^{-iq\cdot r_j}$ is a Fourier transform of the density when particles are treated as points. The structure factor is a Fourier transform of $g(r)$ so the same reasoning follows that as temperature decreases, the peaks become sharper, which can be seen in Fig. 3.3
3.1. PAIR CORRELATION FUNCTION $G(R)$

Figure 3.3: The structure factor at a variety of temperatures from low to high of bulk PEO and PMMA.

From this figure, we can see that the nearest neighbor periodicity is at wave vector, $q = 1.48\text{Å}^{-1}$ and $q = 1.5\text{Å}^{-1}$ for PEO. These locations are significant since they are the $q$ values where dynamical correlations are usually measured.
3.2 Persistence Length

Chain flexibility is a key molecular feature that is known to affect shifts in glass transition temperature. To characterize the chain flexibility we calculate the persistence length of PEO and PMMA in bulk and film. To obtain the persistence length first evaluate the bond orientation correlation between any two monomers along the same chain,

\[ \langle \cos \theta(s) \rangle = \langle \mathbf{u}(r) \mathbf{u}(0) \rangle \]  

(3.5)

where \[ \mathbf{u}(r_i) = \mathbf{r}_i - \mathbf{r}_0 \]. By calculating this correlation function for a variety of temperatures, which can be observed in Fig. 3.4, we see that temperature weakly impacts the correlation between bond orientation and monomer separation.

![Figure 3.4](image)

Figure 3.4: This plot shows the changes in the correlation between the \( \cos \theta \) formed between two monomers along the same chain.
The behavior of $\langle \cos \theta(s) \rangle$ is usually exponential which allows for a simple definition of persistence length, $l_{ps}$,

$$\langle \cos \theta(s) \rangle = \exp \left( -\frac{s}{l_{ps}} \right), \quad (3.6)$$

where $s$ is the monomer separation, $i - j$. Since this behavior is exponential, we can extract the temperature-dependent persistence length as the separation distance where $\langle \cos \theta(s) \rangle = 1/e$. Since Eq. 3.5 determines the separation in terms of $s$, we multiply separation size by the backbone pair interaction length converting monomer separation to a real length. Recall that the interaction length for PMMA is $\sigma_{AA} = 5.5\text{Å}$ and for PEO $\sigma = 4.3\text{Å}$. 
Figure 3.5: This figure illustrates the persistence length measured in Å as a function of temperature. The temperature has been normalized by $T/T_{g,Bulk}$ to compare the persistence lengths of PEO and PMMA at the same relative temperature.

Since the persistence length is a weakly varying function of $T$, we quantify the flexibility of the chains by averaging the persistence length over the temperature range $T/T_{g,Bulk} = 1.1$ to $1.5$. From the average persistence lengths

Table 3.1: Table of average persistence lengths

<table>
<thead>
<tr>
<th>System</th>
<th>Bulk (Å)</th>
<th>Film (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO</td>
<td>$7.06 \pm 0.02$</td>
<td>$6.9 \pm 0.01$</td>
</tr>
<tr>
<td>PMMA</td>
<td>$15.53 \pm 0.49$</td>
<td>$15.37 \pm 0.40$</td>
</tr>
</tbody>
</table>
listed in Table 3.1, it is clear that PMMA is much stiffer than PEO.

### 3.3 Density Profile

Investigating density as a function of distance from the substrate reveals the monomer organization throughout the film. Therefore, by looking at the density, we are able to relate molecular structure to packing.

![Graph showing density profile of PMMA and PEO](image)

**Figure 3.6:** The density profile of PMMA and PEO is plotted as a function of distance from the substrate measured in Å. (a) The black dashed curve represents the density profile of the film as a whole, the density of just the backbone is plotted in gray, and the density of the side groups is in yellow. In panel (b), the density profile of PEO.
As observed in Fig. 3.6, the maximum density of the PEO is $\rho = 4.5\, \text{g/cm}^3$ which is much larger than the peak density of PMMA at $\rho = 3.7\, \text{g/cm}^3$. PMMA has two peaks near the substrate, a minor peak that occurs at $z = 3.4\, \text{Å}$ and a larger peak farther up the film at $z = 7.5\, \text{Å}$ however, PEO has one clear major peak that occurs at $z = 4.5\, \text{Å}$. By distinguishing between the PMMA backbone and side group density, it becomes clear that the minor peak at $z = 3.5\, \text{Å}$ has a large contribution from the side groups while the major peak at $z = 7.5\, \text{Å}$ is solely comprised of backbone beads. This indicates that the side group beads align themselves along the substrate, pushing the backbone beads higher up the film. This preferential organization is enthalpically driven due to the higher polymer-substrate interaction between the substrate and the side groups compared to the substrate-backbone interaction strength which are listed in Table 2.5 which were derived from Eq. 2.10.

3.4 Summary of Effects on Structure

From the pair correlation function $g(r)$ and the structure factor $S(q)$, the presence of the side group and the different potential interaction lengths affect the overall structure in bulk. Since these parameters are unchanged under confinement, this structure remains the same in film. The persistence length is nearly twice as long for PMMA than for PEO, indicating PMMA has a more rigid backbone. The difference in density profiles suggests that PEO has a higher packing efficiency since the chains are allowed to pack closer and more densely near the attractive substrate.
Chapter 4

Impact of Molecular Architecture on Dynamics in Thin films

In this chapter I will discuss the dynamics of the PEO and PMMA ultrathin films. In doing so, I will examine the dynamics in three regions of the film:

• the polymer-air interface sometimes referred to as the free surface in this document. This region is the top 10Å of the film.

• the interior which is the middle of the film (≈ 30Å).

• the substrate-polymer interface, which is the bottom 10Å of the film.

By separating the dynamics into three regions, we are able to understand the interfaces affect on the overall film dynamics.
4.1 Mean-Square Displacement

The glass transition is a consequence of the slowdown of particles, therefore quantifying the mobility of particles in each of the three regions is a valuable reference point. The mean-square displacement (MSD) $\langle r^2(t) \rangle$ is one method to understand the motion defined as,

$$\langle r^2(t) \rangle = \frac{1}{N} \langle |r_i(t) - r_i(0)|^2 \rangle,$$

(4.1)

where $N$ is the number of monomers and $r_i$ is the position of monomer $i$. There are three distinct regimes of the MSD for glass-forming liquids: ballistic at small timescales, sub-diffusive and diffusive at large timescales. Within the ballistic regime, the displacements are equal to $\langle v^2 \rangle t^2 = \frac{3k_BT}{m} t^2 = 3T t^2$ in reduced units of $m = k_b = 1 \ [44]$. When there are substantial caging

Figure 4.1: For this chapter, all plots of the substrate layer (bottom 10 Å) are in blue, the interior which is $\approx 30\text{Å}$ (middle layer) in black and the free interface (top 10 Å) in red.
effects, $\langle v^2 \rangle t^2$ plateaus between the ballistic and sub-diffusive, best seen in the substrate curves of Fig. 4.2. The diffusive regime can be characterized by the relation,

$$D = \frac{\langle r^2(t) \rangle}{6t},$$  \hspace{1cm} (4.2)

where $D$ is the diffusion coefficient. Due to computational constraints, these systems could not access the timescales necessary for diffusive motion. By evaluating the MSD in the three different regions of the film, we can see how the interfaces affect mobility.
Figure 4.2: Mean-square displacement of PEO and PMMA emphasizing the ballistic regime with slope 2 and the sub-diffusive regime with slope $\gamma$ on a log-log plot at temperature $T/T_g = 1.11$. A transition into the caged regime is apparent in the substrate curves (blue) that occurs due to neighbor crowding. At the intermediate timescale, between short and long-time scales past the relaxation time, is the sub-diffusive regime.

Past the ballistic regime, at small timescales where all particles have the same velocity, monomers in the free surface are allowed to move the fastest. Monomers in the substrate layer move the slowest and the interior monomers move with some velocity in between the substrate and free surface velocity. Examining the “caged” section of the curve, the MSD plateau is emphasized in the substrate layer due to reduced mobility caused by the
attractive substrate. For clarification, the “caged” regime is, for example, the region of the PEO substrate curve between $10^0$ ps and $10^3$ ps in Fig. 4.2. For the sub-diffusive regime, we can quantify the behavior of the MSD by fitting the curve to the power law relation, $At^\gamma$ and comparing the slope $\gamma$ on a log-log plot. At temperature $T/T_g = 1.11$, the free surface layer has slope 0.58 and 0.44 for PEO and PMMA, respectively. For the substrate layer, $\gamma = 0.59$ and 0.54 for PEO and PMMA, respectively. These values are within the bounds of the expected slope from the Zimm and Rouse models, where $\langle r^2 \rangle \propto t^{2/3}$ and $\propto t^{1/2}$, respectively [45].

Since the side group and backbone have different masses it is instructive to look at the mean-square displacement of the two beads separately.

![Figure 4.3: The MSD of the side group (yellow) and backbone (gray).](image)

The side groups have a larger MSD than the backbone which is a result of the side group having a smaller mass and having a more flexible bond with the backbone than the backbone-backbone bond. At larger timescales, these MSD should nearly converge, since displacement is ultimately controlled by the center of mass motion of the chains.
4.2 Intermediate Scattering Function $F_{\text{self}}(q, t)$

The incoherent intermediate scattering function is the self part of the intermediate scattering function (ISF), $F_s(q, t)$. The ISF is the time-dependent density-density correlation function, corresponding to a correlation of the number density fluctuations characterizing the similarity in structure over time $t$ at a wave vector $q$. $F_s(q, t)$ directly relates to experimental inelastic neutron scattering, making it valuable for a comparison between simulation and experiment. The ISF is defined as,

$$F_s(q, t) = \frac{1}{N} \left\langle \sum_{j=1}^{N} \exp[iq \cdot (r_j(t) - r_j(0))] \right\rangle,$$

where $r_j$ is the position of the $j^{th}$ particle at time $t$ and $N$ is the total number of monomers. $F_s(q, t)$ has been evaluated at $q_0 = 1.48\,\text{Å}^{-1}$ for PMMA and $q_0 = 1.5\,\text{Å}^{-1}$ for PEO, corresponding to the nearest neighbor periodicity retrieved from the first peak of $S(q)$ in Fig. 3.3. When $F_s(q, t) = 1.0$, that is a perfect correlation between a particle’s position at time $t$ and its initial position at $t = 0$. $F_s(q, t)$ decreases with increasing time, and goes to zero when the position is random relative to the starting location. As discussed in Section 4.1, the caging phenomena can also be seen in $F_s(q, t)$. At high temperatures, $F_s(q, t)$ is a simple exponential decay because monomers have enough thermal energy to avoid being trapped by neighboring particles. However, at low temperatures, a two step $\alpha$- and $\beta$-relaxation process becomes distinguishable from $F_s(q, t)$. As mentioned in Section 1.2, $\alpha$-relaxation is related to the motion of particles leaving the cage formed by neighboring par-
particles whereas $\beta$-relaxation is when the vibrational motion of particles within the cage ceases. The timescale for $\alpha$-relaxation is longer than $\beta$-relaxation since vibrational motion ceases earlier than the cooperative motion associated with $\alpha$-relaxation. Since these relaxations have two different timescales, they result in a clear two-step relaxation process at low temperatures.

![Figure 4.4](image.png)

Figure 4.4: At high temperatures (red), the ISF rapidly decays to zero due to high thermal energy. However, for low temperatures (yellow) there is a slow two-step decay process due to caging effects.

Our interest is to quantify the relaxation process in the three different regions of the film. Since $F_s(q, t)$ can be defined for individual particles, we can evaluated $F_s(q, t)$ of the particles whose positions are within a region at a certain time $t$. 
4.2. INTERMEDIATE SCATTERING FUNCTION $F_{\text{SELF}}(Q, T)$

Figure 4.5: Intermediate Scattering Function of PEO and PMMA at temperature $T/T_{g, \text{Bulk}} = 1.1$ in three different regions of the film: near the substrate (blue), the interior (black) and the free surface (red) with the gray dashed line is the ISF for the bulk material. The free surface has the fastest relaxation, followed by the bulk-like interior and then the substrate in blue relaxes the slowest. This trend is evident in both PEO and PMMA.

Fig. 4.5 shows that PEO and PMMA have the same trend in relaxation with the free surface relaxing the fastest, the substrate relaxing the slowest and the interior relaxing at the same rate as the bulk material. This result is in agreement with the MSD that we saw in Fig. 4.2, where the most
mobile region is the surface, the least mobile region is the substrate layer and the interior is nearly bulk-like. The fast relaxation process of the free surface effectively ‘cancels out’ the slow relaxation process of the substrate. Consequently, the overall film relaxation is nearly identical to the bulk.

4.3 Relaxation Time \( \tau \)

The alpha relaxation (excluding the vibrational relaxation) can generally be described by a stretch exponential form,

\[
F_s(q,t) = A \exp \left[ - \left( \frac{t}{\tau} \right)^{\beta} \right]
\]  \hspace{1cm} (4.4)

This arises from the fact that glass-forming liquids are dynamically heterogeneous (further explained in Section 4.5). Therefore the overall structural relaxation is a superposition of many exponential relaxations with different characteristic timescales. Given this description, we define the relaxation time \( \tau \) as the time when \( F_s(q,t) \) reaches the fixed value, \( 1/e \). Defining the relaxation time as a function of temperature is one method of obtaining the glass transition temperature. This method is comparable to the experimental procedure inelastic neutron scattering used to measure \( T_g \). As discussed in Section 1.1, for high temperatures the temperature-dependent relaxation time can be described by the Arrhenius relationship in Eq. 1.1. However, as temperature decreases, the activation free energy is no longer constant causing a large increase in relaxation time within small ranges of temperatures. The relaxation time at low temperatures, below \( T_A \) where the Arrhenius be-
behavior ceases, can be described by the Vogel-Fulcher-Tammann relation [6, 46],

$$\tau = \tau_0 \exp \left[ \frac{D T_0}{T - T_0} \right].$$

The VFT relation, though largely empirical, is very useful to describe the T dependence of nearly all glass forming fluids. The experimental convention is to define $T_g$ as $\tau(T_g) = 100$ ns, however, those timescales are computationally inaccessible. The glass transition temperature can be extrapolated from the VFT equation where $\tau(T_g) = 10^3$ ps. Nonetheless, the computational definition only slightly varies from the experimental definition due to the steepness of the relaxation approaching $T_g$. The structure factor can also be used to describe the wave vector $q$ dependence of the relaxation time by the deGennes narrowing relation [47], $\tau(q) \propto S(q)/q^2$. However, in for this study we use the VFT relationship to fit our data.
Figure 4.6: This figure shows the validity of the Vogel-Fulcher-Tammann relation between relaxation time and temperature. In yellow symbols are data collected from a film simulation and the orange line is the VFT fit. The conventional computational definition of the glass transition temperature is $\tau(T_g) = 10^3$ ps. Therefore the temperature for which the fit and the dotted red line intersect is $T_g$.

We can extract the glass transition temperature for each region using the VFT fit, which is reported in Table 4.1. It must be emphasized that in these fits we only used data where $\tau < 10^3$ to ensure the exclusion of non-equilibrium points.
4.3. RELAXATION TIME $\tau$

Table 4.1: Glass Transition Temperature, $T_g$, of Bulk Polymer, Ultrathin Films, and Film Regions from VFT. Note that all temperatures are expressed in Kelvin and normalized $T_g$ is $\frac{T}{T_{g,Bulk}}$, where PEO bulk $T_g = 270K$ and PMMA bulk $T_g = 389K$.

<table>
<thead>
<tr>
<th>Region</th>
<th>PEO</th>
<th>PMMA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_g$ (K)</td>
<td>$T_g/T_{g,Bulk}$</td>
</tr>
<tr>
<td>Film</td>
<td>266</td>
<td>0.99</td>
</tr>
<tr>
<td>Free</td>
<td>244</td>
<td>0.89</td>
</tr>
<tr>
<td>Interior</td>
<td>269</td>
<td>0.99</td>
</tr>
<tr>
<td>Substrate</td>
<td>295</td>
<td>1.11</td>
</tr>
</tbody>
</table>

Both PEO and PMMA experience exceptionally small reductions in overall film $T_g$ and interior $T_g$, such that the PEO film $T_g$ is only $4K$ under the calculated bulk $T_g$ and PMMA experiences an overall film $T_g$ reduction of just
4.3. RELAXATION TIME $\tau$

$7K$. The free surface layers undergo a larger reduction in $T_g$ because the free surface allows for better monomer rearrangement leading to a faster relaxation time and lower $T_g$. In the substrate layer PEO, experiences a slightly larger enhancement relative to bulk $T_g$ than PMMA which can be linked to it’s higher packing efficiency. Understanding how each region behaves with respect to the bulk material indicates how interfacial effects contribute to the overall reduction of $T_g$.

Since PMMA has a higher $T_g$ than PEO, it is clear that $F_s(q,t)$ for PMMA must take longer to relax to the value $1/e$ than $F_s(q,t)$ for PEO at the same temperature. Therefore, to make a meaningful comparison between PEO and PMMA we must scale temperature by $T_g$ to ensure the two systems are in similar stages of the liquid-glass transition. Scaling by $T_g$ exposes the differences in the curvature and rate of change of $\tau(T)$ for the two different polymers.
4.3. RELAXATION TIME $\tau$

PEO and PMMA experience similar shifts in relaxation time for each region. This indicates that although there are significant structural differences between PEO and PMMA, when examined over the same relative temperature range they relax at the same rate for the overall film and within each region.

Looking at relaxation time as a function of distance from the substrate,
4.3. RELAXATION TIME $\tau$

$z$, we can explore how organization effects relaxation time across the film. Referring back to the density profile, Fig. 3.6, we can see that near the substrate there is an increase in side group beads, this increase is reflected in the relaxation time near the substrate in Fig. 4.9 below.

Figure 4.9: Evaluated at $T/T_g = 1.11$, the relaxation time profile of PMMA (a) and PEO (b) show how relaxation time varies as a function of distance from the substrate.

In panel (a) of Fig. 4.9, the relaxation time is enhanced for the side group beads within the first 4.5Å of the film. The increased crowding at this distance caused the relaxation time of the side group beads to increase. As a consequence of the preferential organization, the backbone density de-
creases at $z = 4.5\,\text{Å}$ but becomes significantly enhanced at $10\,\text{Å}$ resulting in a reduction in backbone relaxation time at $z = 4.5\,\text{Å}$ but a large increase in $\tau$ at $z = 10\,\text{Å}$. The combination of these two effects, drags the overall relaxation time down at $z = 4.5\,\text{Å}$ but up at $z = 10\,\text{Å}$. For PEO, since there is no competition between the side group and backbone, the relaxation time profile follows the expected trend of steadily increasing as you approach the substrate from the interior. In regions where there is a normal organization amongst the backbone and side group beads within the film, exemplary in the interior, the side group bead relaxation is faster which supports what was seen in the mean-square displacements of the side group and backbone.

### 4.4 Fragility

In Section 4.3, we discussed the drastic change in segmental relaxation time of polymeric materials in a narrow temperature range. Angell [10, 48] introduced fragility to quantify the steepness of the temperature dependence of viscosity. Strong liquids do not exhibit the large changes in viscosity that are seen in fragile liquids. Our study aims to see how the fragility changes within each region and how these regions contribute to the overall film fragility. In order to do this, we cannot use the fragility index $m$ (Eq. 1.2) evaluated at $T_g$, since each region has a different glass transition temperature. Instead, we use the parameter $D$ from the VFT relation from Eq. 4.5. For some intuition for $D$, if two different temperature-dependent relaxation curves had the same VFT parameters except for $D$, the curve where $D$ is larger would have a steeper slope around $T_g$. The usefulness of implementing $D$ instead
of $m$ is illustrated by substituting $\tau$ from Eq. 4.5 into Eq. 1.2.

$$
m = \left. \frac{\partial \ln \tau}{\partial (T_g/T)} \right|_{T=T_g}
= \left. \frac{\partial}{\partial (T_g/T)} \left( \ln \tau_0 + DT_0 \left( \frac{T-T_0}{T} \right) \right) \right|_{T=T_g} \tag{4.6}
$$

At this step, we can switch from taking the derivative with respect to $T_g/T$ to $T$.

$$
= \left. \frac{T^2}{T_g} \frac{\partial}{\partial T} \left( \ln \tau_0 + DT_0 \left( \frac{T-T_0}{T} \right) \right) \right|_{T=T_g}
= \left. \frac{T^2 DT_0}{T_g (T-T_0)^2} \right|_{T=T_g}
= \frac{DT_g T_0}{(T_g - T_0)^2} \tag{4.7}
$$

Therefore, $m \propto D$ where higher values of $D$ correspond to more fragile glass formers.

**Table 4.2: The fragility parameter $D$ from the VFT equation**

<table>
<thead>
<tr>
<th>Region</th>
<th>PEO</th>
<th>PMMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Film</td>
<td>3.2</td>
<td>3.3</td>
</tr>
<tr>
<td>Free</td>
<td>1.2</td>
<td>1.4</td>
</tr>
<tr>
<td>Substrate</td>
<td>3.6</td>
<td>7.8</td>
</tr>
</tbody>
</table>

The parameter $D$ suggests that PMMA is just slightly more fragile than PEO at the free surface and for the entire film. However, $D$ also reveals that at the substrate, PMMA is much more fragile than PEO suggesting that PMMA is more sensitive to the substrate.
Another method of understanding fragility without using the $T_g$ dependent fragility index $m$ (Eq. 1.2) is to plot fragility as a function of temperature using the function,

$$m(T) = \frac{1}{T} \frac{d\ln \tau}{d(1/T)}$$  \hspace{1cm} (4.8)

By quantifying fragility without using $T_g$ we are able to directly compare the steepness of the temperature dependent relaxation time of the different regions and of the two materials.

![Free Interface](image.png)

Figure 4.10: Panel (a) is the temperature dependent fragility $m(T)$. PMMA is more fragile than PEO at the free interface. In the inset (b) PEO experiences a large fragility reduction compared to the bulk material. PEO is nearly twice as strong at the free interface than bulk.

PMMA is more fragile than PEO at the free surface due to the chain rigidity and existence of the side group frustrating packing. The free sur-
face for both materials is stronger than the bulk material due to the lower energy barrier to rearrange. The normalized fragility, $m/m_{\text{bulk}}$, of PMMA experiences larger temperature variations than PEO due to the increasing constraints of motion as temperature decreases caused by the chain rigidity and bulkiness of the side groups. This result is in agreement with the free surface $D$ values in Table 4.2.

Figure 4.11: (a) $m(T)$ at in the substrate layer is similar for PEO and PMMA and in the inset (b) both experience a similar enhancement when compared to bulk.

However, near the substrate the behavior of the two curves is not as clear. From $m(T)$, it seems that the fragility near the substrate for PEO and PMMA are similar.
4.5 Dynamical Heterogeneity

Approaching the glass transition, glass-forming fluids universally exhibit the phenomenon of dynamic heterogeneity. This means over time, as the liquid is cooled towards the glass transition temperature, the system experiences a dramatic kinetic slowdown as mentioned in Chapter 1. During this slowdown, regions within the melt can have drastically different dynamics. The cooperative behavior of the molecular motion is one of the distinguishing features of liquids approaching their glass transition. On the approach to $T_g$, particle movement in local regions of the material becomes correlated. This effect is known as dynamical heterogeneity. [49]
Particles with similar mobilities are spatially correlated as seen in Fig. 4.12. Although we that glass-forming liquids experience dynamical heterogeneity, there are still many questions to be answered about it such as, why can particles with high mobility can be only a few nanometers away from particles with orders of magnitude lower mobilities and how these particles become spatially correlated at all.
4.5. DYNAMICAL HETEROGENEITY

4.5.1 Non-Gaussian Parameter

In a simple fluid, motion is dynamically homogeneous and is characterized by Brownian motion. Brownian, or diffusive motion, is characterized by a normal (or Gaussian) distribution of molecular displacements. Accordingly, one simple measure of dynamic heterogeneity is the non-Gaussian parameter, $\alpha_2$. If we define a function $G_s(r, t)$ as the probability of a single particle moving a distance $r$ in time $t$ and assume Gaussian behavior then it has the form,

$$G_s(r, t) = (4\pi \rho(t))^{-3/2} \exp \frac{r^2}{4\rho(t)},$$  

where $\rho(t)$ is the number density. From this form, we obtain the following relations:

$$\langle r^2 \rangle = 6\rho(t)$$

$$\langle r^{2n} \rangle = C_n \langle r^2 \rangle^n$$  

$$C_n = 1 \times 3 \times 5 \times 7 \cdots (2n + 1)/3^n,$$

for $n = 1, 2, 3, \cdots$. Therefore, if $G_s(r, t)$ deviates from Gaussian behavior, it can be expressed in terms of the function,

$$\alpha_n = \frac{\langle r^{2n} \rangle}{C_n \langle r^2 \rangle^n} - 1$$  

If $G_s(r, t)$ is not Gaussian, then term $n = 2$ is the first term that will not vanish. This is how the non-Gaussian parameter $\alpha_2$ is defined,

$$\alpha_2 = \frac{3 \langle r^4(t) \rangle}{5 \langle r^2(t) \rangle^2} - 1$$
where $\langle r^2(t) \rangle$ is the mean-square displacement and $\langle r^4(t) \rangle$ is the fourth moment of displacement. [51]

![Graph](image)

Figure 4.13: Non-Gaussian parameter of PEO films for a range of temperatures.

For small timescales where motion is ballistic, $\alpha_2=0$ since velocities follow a Maxwellian distribution which is Gaussian [51]. However, during the intermediate timescales, where caging effects are prominent, $\alpha_2$ experiences a peak. Caging can create local correlated motion which deviates from the Gaussian behavior. Since caging becomes enhanced at lower temperatures, in Figs. 4.13 and 4.14 the peaks of $\alpha_2$ increase and occur at larger timescales with decreasing temperature.

4.5. DYNAMICAL HETEROGENEITY

The degree of heterogeneity of PEO and the side groups of PMMA are similar, however, the backbone of PMMA experiences significantly less non-Gaussian motion. It is possible that the higher rigidity of the backbone negatively impacts the dynamical heterogeneity however, $\alpha_2$ only informs us on the degree of heterogeneity not what causes it. Therefore, we must investigate further to understand why the two materials experience different levels of non-Gaussian motion.

4.5.2 String-like Cooperative Motion

The non-Gaussian parameter is a simple and useful indicator that molecular motion is more complicated, but does not inform us about precisely what features of the motion give rise to non-Gaussian displacements. The
link between the two is collective motion. When particles become spatially constrained by the caging effect, monomers rely on cooperative rearrangement. Adam-Gibbs (AG) [52] theory predicts that within glass-forming liquids, there are regions of monomers that are incapable of moving independent of their surroundings called cooperatively rearranging regions (CRR). However, AG theory gave no way of identifying CRR or a molecular description of them. Later, Donati et al. [53] identified that within glass-forming materials there exist particles that move in a string-like behavior illustrated in Fig 4.15 but had not yet made the link to the CRR from AG theory.

![String-like cooperative motion schematic](image)

**Figure 4.15:** A schematic of string-like cooperative motion with string size 7 monomers. The red beads indicate the initial position of the monomers and the tip of the vectors indicates the new position after time $t_L$, which is the characteristic timescale that $L(t)$, string length, is at a maximum. This figure was reproduced from Ref. [54]

Since string-like behavior is most prominent in regions that are highly mobile we must determine what particles fall in the category of highly mobile. When comparing the actual $G_s(r, t)$ with the assumed Gaussian behavior (Eq. 4.9), there are particles that have moved significantly farther than what the Gaussian behavior predicts after a time $t^*$ which corresponds to the time $\alpha_2(t)$ reaches a maximum. From several studies [55–57] that use this definition of mobile particles, the number of mobile particles constitutes 5 – 7% of total
particles at any temperature. Therefore, to probe string-like motion, strings are specifically defined within the top 6.5% of mobile particles, if particle \(i\) and \(j\) meet the criteria,

\[
\min[|\mathbf{r}_i(t) - \mathbf{r}_j(0)|, |\mathbf{r}_i(0) - \mathbf{r}_j(t)|] < \delta = 0.45
\]

where \(\mathbf{r}\) is the position of a particle. Employing this definition to probe the temperature dependence of strings, we can see that with increasing temperature the string size decreases. At high temperatures, particles no longer rely on cooperative rearrangement to move within the material.

Figure 4.16: The string length, \(\langle L(t) \rangle\), as a function of time. \(\langle L(t) \rangle\) decreases with temperature due to the decreased need to move cooperatively. PEO has much larger string sizes than PMMA because the simple structure of PEO allows it to replace a neighboring monomer much easier than PMMA beads can replace each other.

Comparing the average string lengths of PEO to PMMA, at high temperatures the string lengths are roughly the same, however, as temperature decreases \(\langle L(t) \rangle\) for PEO becomes much larger than PMMA since the backbone is stiffer and the string-like motion becomes difficult. The PMMA string
length is averaged over all possible replacements: backbone-backbone, side
group-backbone and side group-side group. By separating these replacements
out, we can understand how they contribute to the total. This result is in
agreement with the $\alpha_2$ results since reduced dynamical heterogeneity would
correspond with less cooperative motion. Since the strings are smaller for
PMMA, we have less cooperative motion.

Figure 4.17: (a) The backbone-backbone strings have two features, one at
small timescales linked to vibrational motion and one at larger timescales
that is the cooperative motion due to caging.(b) The average side group-side
group string length $\langle L(t) \rangle$ is calculated over the top 6.5% most mobile particles therefore to
understand the origin of the features of the total $\langle L(t) \rangle$ in Fig. 4.16 we
need to investigate the MSD of the side group and backbone at different
temperatures.
Figure 4.18: In the dotted circles are times when the MSD of the side group and backbone are similar. These are the timescales when features of the backbone $\langle L(t) \rangle$ (Fig. 4.17(a)) appear in the total $\langle L(t) \rangle$ in Fig. 4.16(b)

At high temperatures, the total string length of PMMA is dominated by the side groups since they are faster than the backbone. The MSD of the side group and the backbone are similar at long timescales where $\langle L(t) \rangle$ is small for both the backbone and side group so, a unique feature in the total cannot be seen. However, at low temperatures, the two features of the backbone $\langle L(t) \rangle$ is apparent in the total $\langle L(t) \rangle$ since these peaks occur on the same timescales when the MSD of the side group and backbone are similar.
Figure 4.19: (a) Peak string length $L_{\text{max}}$ as a function of normalized temperature. The average string length for all temperatures is larger for PEO than PMMA. (b) The time that $L_{\text{max}}$ occurs as a function of normalized temperature. Here we can see that the time these peaks occur are very similar for both systems however it takes PMMA slightly longer to reach $L_{\text{max}}$, especially as temperature decreases.

Plotting the peak $\langle L(t) \rangle$, $L_{\text{max}}$, as a function of temperature we see clearly that the string length for all temperatures is larger for PEO than for PMMA. PMMA takes longer to reach $L_{\text{max}}$ seen in the quantity $t_L$, which deviates from $t_L$ for PEO as temperature decreases. Due to the complex architecture of PMMA, string-like motion is difficult even at low temperatures when motion is typically cooperative.
4.5.3 Adam-Gibbs Relation

With the prediction of CRR, AG theory introduced the importance of a dynamical size scale long before dynamical heterogeneity was an accepted phenomenology. AG theory argues that upon cooling towards \( T_g \), motion becomes dominated by CRR causing the activation barrier \( \Delta F \) to be extensive in \( z \), the number of rearranging monomers in a CRR, resulting in the relationship,

\[
\tau \sim \exp[z \Delta F_A / T],
\]

(4.14)

where \( T \) is temperature and \( \Delta F_A \) is the activation barrier at high temperatures \( (T > T_A) \). According to work by Starr et al. [58], the best mass to use for \( z \) is the one defined by the max string length, \( z = L_{max} \). From this our relationship becomes,

\[
\tau \sim \exp[L_{max} \Delta F_A / T],
\]

(4.15)

where \( \Delta F_A = \Delta H - T \Delta S \).
4.6. SUMMARY OF EFFECTS ON DYNAMICS

The dynamical properties are similar between PEO and PMMA despite their differing molecular architecture. From $F_s(q, t)$, we know PMMA has a longer relaxation process at the same temperature and thus a higher $T_g$ than PEO.
4.6. SUMMARY OF EFFECTS ON DYNAMICS

However, once relaxation time, $\tau(T)$ is normalized by the bulk glass transition temperature $\tau(T/T_{g,Bulk})$, both PEO and PMMA have similar rates in relaxation at the same $T/T_g$ indicating that the molecular architecture only weakly impacts the relaxation process. However, if we investigate the relaxation profile of each film $\tau(z)$ (see Fig. 4.9), we see how the monomer organization affects relaxation times near the substrate. The preferential packing of PMMA beads described in Chapter 3 results in the relaxation time of the layer nearest the substrate (below 5.0 Å away from the substrate) is faster than the layer above that, from 5.0 to 10 Å. This behavior is atypical since the dynamics tend to slow down as particles approach the substrate. In PEO, where there is no side group, the behavior the relaxation profile follows the expected trend of increasing relaxation time as $z$ decreases.

To quantify fragility without using the fragility index $m$ defined in Eq. 1.2, we use the parameter $D$ from the VFT relationship (Eq. 4.5). From $D$ we can see that the overall film fragilities of PEO and PMMA are similar. However, when examining the fragilities within the three regions of the film we see that the substrate layer has a $D$ value that is nearly twice as large as PEO. This indicates that PMMA has a much higher fragility in the substrate layer and is more sensitive to the substrate than PEO.

Dynamical heterogeneity is a hallmark of glass-forming liquids. We evaluate two quantities that probe dynamical heterogeneity: the non-Gaussian parameter, $\alpha_2$, and string length $\langle L(t) \rangle$. From $\alpha_2$, we observed that PEO has a similar degree of non-Gaussian behavior as the side group of PMMA. However, the backbone of PMMA behaves much more Gaussian than the side group. Examining string length allow us to see how molecular motion
relates to dynamical heterogeneity. We observed that for the same normalized temperature, $T/T_g$, PEO has larger string lengths, $L_{max}$ that occur at shorter timescales, $t_L$, than PMMA.
Chapter 5

The Effect of Substrate Interaction Strength on PEO and PMMA Ultrathin Films

The role of interfacial dynamics becomes increasingly important to the overall dynamics of ultrathin films as film height decreases. Therefore, for supported films the role of the substrate is critical. The work described in Chapters 3 and 4 employed a silicon substrate with a nearly neutral substrate-polymer interaction, seen in Table 5.1.

Table 5.1: Non-bonded Monomer Interaction Strength

<table>
<thead>
<tr>
<th>System</th>
<th>Bead</th>
<th>$\epsilon_{ps}$</th>
<th>$\epsilon_{pp}$</th>
<th>$\epsilon_{ps}/\epsilon_{pp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO</td>
<td></td>
<td>0.98</td>
<td>0.81</td>
<td>1.2</td>
</tr>
<tr>
<td>PMMA</td>
<td>sA</td>
<td>0.5</td>
<td>0.46</td>
<td>0.92</td>
</tr>
<tr>
<td></td>
<td>sB</td>
<td>1.39</td>
<td>1.5</td>
<td>0.93</td>
</tr>
</tbody>
</table>
The ratio $\epsilon \equiv \epsilon_{ps}/\epsilon_{pp} \approx 1.0$ for both PEO and PMMA. From the literature we know that with neutrally interacting substrates, $T_g$ weakly varies from the bulk value as seen in Fig. 5.1.

Figure 5.1: From simulations, we know that for strongly interacting substrates as film thickness decreases, there is a large $T_g$ enhancement and as weakly interacting films there is a significant $T_g$ reduction as film height decreases. However for neutrally interacting films, there is relatively no confinement effects seen, with $T_g$ remaining bulk-like. Note that film thickness has been scaled by $\sigma$ where $\sigma$ is defined from the LJ potential. This figure was reproduced from Ref. [59].

In this chapter, our aim is to investigate the dependence of the structure and dynamics of the film on the substrate interaction strength. To achieve this, the polymer interaction strength was doubled for each system and the remaining potential parameters were kept constant. For the remainder of this chapter, the polymer interaction strength used is twice as strong as the $\epsilon_{ps}$ described in Chapter 2 and used for simulations in Chapters 3 and 4. The
shorthand used throughout this chapter is,

\[ \epsilon = 1.0 \rightarrow \epsilon_{ps} \]
\[ \epsilon = 2.0 \rightarrow 2\epsilon_{ps}, \]

where \( \epsilon_{ps} \) is the value listed in Table 5.1.

## 5.1 Structure of Enhanced \( \epsilon_{ps} \) System

As in Chapter 3, we examine the density profile of the two different materials to understand monomer organization and molecular packing within the films.

![Graph of density profile](image)

Figure 5.2: The density profile of PMMA and PEO is plotted as a function of distance from the substrate measured in Å. (a) The film (black dashed), backbone (gray), and side group (yellow) density. The small peak that occurs in the film total is made up of just side group beads while the major peak that appears in the total density is given from the backbone.
The peak of PEO is much greater than the major peak of PMMA density, further indicating that PEO is a more efficient packer. The separation of side groups and backbone beads becomes even more pronounced in the $\epsilon = 2.0$ PMMA system signifying a greater change in structure. When compared to $\epsilon = 1.0$ (see Fig. 5.3), the small peak at $z = 4.5\text{Å}$ actually decreases from $\rho = 1.27 \text{ g/cm}^3$ and shifts to $z = 3.5\text{Å}$ and $\rho = 0.81 \text{ g/cm}^3$. The mass of the side groups is less than the backbone so when the more massive backbone is pushed out, the overall density drops for the first peak and increases the second peak. However, for PEO the organization is the same as the $\epsilon = 1.0$ system except with stronger peaks due to the increased attraction.
Figure 5.3: Comparison of neutral ($\epsilon = 1.0$) and enhanced ($\epsilon = 2.0$) density profiles of (a) PMMA and (b) PEO film. (a) The monomer organization is altered for most of the film due to the change in $\epsilon_{PS}$. (b) The monomer organization is only slightly altered near the substrate.

The monomer organization of the PMMA film is deeply impacted by the increase in substrate interaction. However, there are only small disturbances in the film organization of PEO near the substrate indicating that the PMMA film organization has a higher sensitivity to the substrate than PEO.
5.2 Dynamics of Enhanced $\epsilon_{PS}$ System

A comparison of the relaxation time profiles is critical in understanding the impact of the substrate interaction on the entire film.

Figure 5.4: Relaxation time profile of the neutral substrate film in black and the enhanced substrate in green. The black dotted line indicates the relaxation time of the bulk polymer at the temperature $T/T_g = 1.11$. (a) Relaxation profile of PMMA (b) Relaxation profile of the PMMA backbone (gray) and side group (yellow) beads. (c) Relaxation time profile of PEO.
The effect of the substrate persists further from the substrate for PMMA than it does for PEO, indicating that the substrate interface affects PMMA stronger than it does for PEO. Approaching the substrate from the top of the film, the distance-dependent relaxation time $\tau(z)$ of the $\epsilon = 2.0$ system begins to deviate from the $\epsilon = 1.0$ behavior around $z \approx 30\text{Å}$ whereas PEO seems to have the same behavior as $\epsilon = 1.0$ until distance $z = 18\text{Å}$, roughly the same location the $\epsilon = 1.0$ film begins to deviate from bulk. However, for PMMA, the $\epsilon = 1.0$ film does not start to deviate from bulk until $z = 15\text{Å}$. Referring back to Fig 5.2, the distances where the $\epsilon = 2.0$ $\tau(z)$ behavior deviates from $\epsilon = 1.0$ correspond to the distances were the density profile of $\epsilon = 2.0$ deviates from the profile of the $\epsilon = 1.0$ systems. This indicates the impact of the substrate is much more substantial for PMMA than it is for PEO.

5.2.1 Relaxation Time and Glass Transition Temperature

Increasing the substrate interaction strength produces a larger contribution of the substrate interfacial dynamics to the overall film dynamics. Since the substrate layer has a higher impact on the $\epsilon = 2.0$ systems, the segmental relaxation slows down for the overall film. However, the shifts in film relaxation time for both PEO and PMMA are weak compared to the $\epsilon = 1.0$ and bulk.
Figure 5.5: Normalized relaxation time as a function of normalized temperature. In green, is the enhanced system, $\epsilon = 2.0$ and in black the neutral $\epsilon = 1.0$ film system. There is a small enhancement of relaxation time due to the substrate having a larger impact on overall film dynamics.

Investigating the three regions of the film reveals that the free surface layer is not affected by the increased substrate-polymer interaction strength. On the other hand, dynamics in the substrate layer of PEO drastically slow down as expected. The substrate layer of PMMA was not well-equilibrated on the timescale of the overall film relaxation below 500K.
Figure 5.6: The temperature-dependent relaxation time $\tau(T)$ of (a) PMMA and (b) PEO for the overall film (gray) and each region: free surface (red), interior (black) and substrate layer (blue). The dotted lines and open symbols represent the $\epsilon = 1.0$ systems and the solid line with closed symbols represents the $\epsilon = 2.0$ systems.

The increase in $\epsilon_{ps}$ only increases the film $T_g$ from 270 K to 273 K for PEO and from 389 K to 390 K for PMMA. So increasing the substrate interaction only slightly impacts the overall film dynamics.
5.2. DYNAMICS OF ENHANCED $\epsilon_{PS}$ SYSTEM

Table 5.2: The Glass Transition Temperature of the Total Film and Three Regions

<table>
<thead>
<tr>
<th>Region</th>
<th>PEO</th>
<th>PMMA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_g$ (K)</td>
<td>$T_g$ (K)</td>
</tr>
<tr>
<td></td>
<td>$T_g/T_g,Bulk$</td>
<td>$T_g/T_g,Bulk$</td>
</tr>
<tr>
<td>Film</td>
<td>273</td>
<td>390.3</td>
</tr>
<tr>
<td>Free</td>
<td>245.7</td>
<td>371.1</td>
</tr>
<tr>
<td>Interior</td>
<td>270.8</td>
<td>393.2</td>
</tr>
<tr>
<td>Substrate</td>
<td>350.7</td>
<td></td>
</tr>
</tbody>
</table>

5.2.2 Fragility of Enhanced $\epsilon_{ps}$ System

We saw in Chapter 4 that the $D$ parameter indicates that PEO and PMMA overall film fragilities are very similar. Once $\epsilon_{ps}$ is doubled the fragility parameter $D$ modestly increases from 3.2 to 3.6 for PEO however, PMMA sees a huge increase in $D$ from 3.3 to 5.6. This supports the notion that PMMA has a higher sensitivity to the substrate. For the substrate layer of PEO, $D = 10$, which indicates in order for PMMA to have such a large overall fragility, the fragility of the substrate layer must be much greater than 10 since we saw in Fig. 5.6 that the free layer is not affected by the change in $\epsilon_{ps}$.

Since the substrate layer of PMMA falls out of equilibrium at such a high temperature, we conclude that this layer must have a large fragility. We believe the temperature-dependent relaxation time becomes so steep that we are unable to access the timescales necessary to reach relaxation. The complex molecular architecture of PMMA must make it more sensitive to the substrate interface than the simple backbone structure of PEO.
Chapter 6

Conclusion

Using molecular dynamics simulations of coarse-grained PEO and PMMA models, we were able to investigate the effect of molecular architecture on the structure and dynamics of ultrathin films. PMMA has a persistence length that is nearly twice as long as PEO which is evidence of PMMA having a stiffer backbone than PEO. The presence of the side group and the stiffer backbone prevents PMMA from having a well-organized film displayed in the density profile. There is a preferential organization of the side groups to align along the substrate driven by the side groups having a higher substrate-polymer interaction strength than the backbone. The density profile is also evidence of the packing frustration PMMA experiences confirmed by the ability of PEO monomers to crowd closer and more densely near the substrate than PMMA monomers.

Unlike the structure and organization of the film, the dynamical quantities are only weakly affected by the architectural differences between PMMA and PEO. The glass transition temperature of PEO was less than PMMA.
because PEO undergoes a faster relaxation process at the same temperature. However, once the temperature is scaled by \( T_g \), there are negligible differences in their dynamic behavior. The glass transition temperature of the PEO and PMMA films are only slightly reduced when compared to the bulk \( T_g \). By breaking down the film into different regions, we were able to see the impact of the interfaces on the overall film. The reduction of \( T_g \) in the free surface was balanced by the enhancement in \( T_g \) near the substrate resulting in an overall \( T_g \) of the films that were nearly the same as the bulk \( T_g \).

Another benefit of scaling temperature by \( T_g \) is the ability to compare the fragility of the overall film and each region, which is not possible with just the fragility index, \( m \), defined in Eq. 1.2. We employ the parameter \( D \) from the VFT equation (Eq. 4.5) to probe the leading contribution of the fragility since \( D \propto m \). The values of \( D \) for the overall films of PEO and PMMA suggests sensible fragility behaviors. Examining the interfacial regions, the \( D \) values indicate that the free surface of PEO is just slightly stronger (less fragile) than the free surface of PMMA whereas the substrates have a more pronounced difference. The substrate layer of PMMA has a \( D \) value that is more than twice that of the substrate layer of PEO, suggesting PMMA is more sensitive to the interfaces, especially the substrate interface.

In order to explore the substrate-polymer interaction sensitivity, we conducted another set of supported thin film simulations employing a stronger substrate interaction strength, \( \epsilon_{ps} \). From these simulations, we observe that the substrate effect persists farther from the substrate for PMMA than for PEO, disrupting the monomer organization all the way through the interior layer until nearly the beginning of the free surface layer. The disruption in
the organization is also manifest in the relaxation time profile, $\tau(z)$, causing an increase in relaxation time relative to bulk nearly 30 Å away from the substrate for PMMA and 15 Å from the substrate for PEO. The film $T_g$ was nearly bulk-like for both PEO and PMMA however, when investigating the $T_g$ of the layers we were unable to reach equilibrium in the substrate layer of PMMA. This inability to equilibrate indicates that the relaxation time must rapidly increase upon cooling and exit our window of computationally accessible timescales. If that is a true description of $\tau(T)$ for the substrate, it suggests that the substrate layer of PMMA is much more fragile than the substrate layer of the PEO film. Although we do not see significant differences in the dynamic behavior the PEO and PMMA films, we do observe that PMMA is more sensitive to the interfaces than PEO because of its complex architecture.

As a last remark, our future work aims to understand the reasoning behind the molecular architecture’s weak impact on dynamics by fine-tuning the model parameters like backbone and side group stiffness. Also since the PEO model does not formally have side groups it is difficult to quantify the competing effect between the side group/backbone stiffness. Polymers like polycarbonate (PC) and polyisobutylene (PIB) would be interesting to study because both have side groups but different degrees of backbone-to-sidegroup stiffness ratios leading to different experimentally measured fragilities. By conducting more controlled simulations we wish to uncover more detail on the effect of molecular architecture on dynamical properties.
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