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CONTROL OF POLYMER GLASS FORMATION BEHAVIOUR USING MOLECULAR DILUENTS AND DYNAMIC INTERFACES

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CONTROL OF POLYMER GLASS FORMATION BEHAVIOUR USING
MOLECULAR DILUENTS AND DYNAMIC INTERFACES

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ABSTRACT

The end use application of polymeric materials is mainly determined by their viscosity, thermal stability and processability. These properties are primarily determined by the segmental relaxation time ($\tau_\alpha$) of the polymer and its glass state modulus, which determines its glassy mechanical response. Developing design principles to obtain rational control over these properties would enable fabrication of new polymers or polymer blends with improved thermal stability, enhanced processability and better mechanical robustness of the material.

Introduction of diluents and nanostructuring of the material serve as invaluable tools for altering polymers’ glass transition and associated dynamic and mechanical properties. Besides providing guidelines for technologically important improvements in processability, glassy mechanical properties, and transport behavior, diluent effects and behavior of nanostructured materials can provide insights into the fundamental physics of the glass transition, for example, by elucidating the interrelation between high- and low-frequency structural relaxation processes. It has been previously suggested that there exists a similarity between how diluents and interfaces impact the glass formation behavior of the polymer, raising the possibility that the effects of these two polymer modifications may be separate manifestations of a common set of physics in glass forming polymers.
Here we address several interrelated questions in the understanding of glass formation in polymer/diluent blends and nanostructured polymers. First, what is the relationship between a diluent’s molecular structure and its impact on a polymer’s glass formation behavior? How does this compare to the effect of interfaces? Second, how does the introduction of diluents impact the role of interfaces in modifying polymer glass formation? Third, how does the introduction of interfaces impact metrology of the polymer glass transition? Finally, we address a major open question regarding the role of interfaces in the formation of a new class of ‘ultrastable’ glassy materials.

The major conclusions of this work are as follows. We show how the effect of diluent on polymer glass formation depends on its molecular properties like structure, backbone stiffness, interaction strength with the host polymer etc. These effects are shown to be predicted by a functional form analogous to the one shown in the literature for predicting $T_g$ shifts in nanostructure materials. We further show that these diluents when introduced in nanostructured materials, bring about $T_g$ shifts in a manner which does not correlate completely with the bulk fragility of the material, as previously suggested. We also show that there are confounding variables other than bulk fragility of the material – such as composition gradients, variability in measurement of $T_g$ using different experimental techniques, etc. – that need to be considered when identifying the $T_g$ nanoconfinement effects of the material. We also address this issue of having metrological differences in measuring $T_g$, by establishing appropriate weighting factors to be used while using different experimental techniques to measure $T_g$ of confined materials. Finally, we propose a three layer model of the interface in which a facilitated layer intermediate
between the surface and bulk exhibits enhanced bulk like liquid density which leads to the emergence of exceptional mechanical properties in “ultrastable” glasses.
I dedicate this dissertation to my parents, Aruna Jyothi and Narahari Mangalara, for their constant support and guidance. The constant motivation I received from them helped me focus and achieve greater heights.

Also, this work would not have been possible if not for the contributions from previous researchers who have been working in this field and continuously contributing to the literature. This is my humble effort to add a little more to the existing literature and would like to dedicate this dissertation to all the people that might find this work interesting.
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CHAPTER I
INTRODUCTION

Glassy polymeric materials have been fundamental to developing technology for centuries. These materials find a wide variety of applications in the field of energy storage devices, flexible electronics, food and drug preservation, and many more. Next-generation materials demand the development of new class of glass forming polymers which are mechanically robust and yet are lighter and more flexible. This requires a finely controlled approach to tune polymer glass formation behavior, but the fact remains that the fundamental understanding of glass formation behavior and efficient methods to modify the glass formation behavior are still elusive in the literature.

One of the common methods by which we can tune polymer glass formation behavior and associated mechanical properties is by the introduction of molecular diluents in low volume fraction. They alter the viscosity ($\eta$), segmental relaxation time ($\tau_\alpha$), glass transition temperature ($T_g$), breadth of glass formation or polymer fragility ($m$), and/or Young’s modulus of the host polymer matrix. These diluents are ubiquitous and are commonly used in our daily lives. For example, addition of plasticizer significantly reduces the glass transition temperature ($T_g$) of PVC below room temperature, enabling it to be used as a soft and flexible material, whereas pure PVC is hard and brittle at room
temperature. Despite the ubiquity of the diluents for tuning properties of glassy polymers, the precise molecular mechanism controlling these alterations is not very well understood. Prior literature indicates that the molecular properties of diluents, like size, flexibility, cohesive energy, and thermodynamic properties like temperature and concentration, play a crucial role in determining the effects that diluents have on polymer properties. Since diluents’ effects on polymers’ segmental dynamics and mechanical response are tied to their impact on polymer glass-formation physics\textsuperscript{1,2}, these open questions are closely related to the generally poor understanding of the glass transition itself. Apart from improving polymers’ performance, introduction of molecular diluents has been employed as a method of probing fundamental relationships between different aspects of the dynamics of glass-forming liquids\textsuperscript{3–8}. A richer understanding and classification of diluents’ effects and their dependence on diluent molecular properties would therefore be of considerable value in more rationally understanding and controlling glass formation, segmental dynamics, and mechanical behavior of the host polymer.

In recent literature, polymer diluents are classified into two broad classes based on the way they affect slow dynamics ($\eta$, $\tau_\alpha$, $T_g$, and $m$) and fast dynamics (high frequency shear modulus, $G_\infty$) of the host polymer. Plasticizers are additives which decrease the glass-state modulus and $T_g$ of the polymer to which they are added\textsuperscript{1,2}. The softening effect of plasticizer is used to improve the formability of a polymer. On the other hand, antiplasticizers simultaneously improve a polymer’s processability (decrease $T_g$ and $m$) and increase its glass-state modulus\textsuperscript{1,6,9–11}. Other additives can enhance a polymer’s glass transition\textsuperscript{12}, thereby expanding its applicability to higher-temperature applications, or can impose strongly temperature-dependent alterations to a polymer’s modulus\textsuperscript{7} or viscosity.
The stiffening effect of antiplasticizers is widely exploited in protein preservation and they serve as widely used additives in this field. We can see from the literature on this topic that there are contrasting definitions of an antiplasticizer, and this indicates that classification of additives is not distinct and clear. It also suggests that slow and fast dynamics can be decoupled and there is apparently a lack of evidence that they are correlated. This is also complicated by the fact that the effect of additives on fast dynamics is strongly dependent on temperature.

Several previous studies have suggested a nontrivial interplay between diluent and interface effects on polymer glass formation, raising the possibility that the effects of these two polymer modifications may be separate manifestations of a common set of physics in glass forming polymers. The introduction of molecular diluents into nanostructured materials can significantly alter \( T_g \)-nanoconfinement effects. Previous studies\(^\text{14,15}\) have shown that decreasing the bulk state fragility of a material using small molecule diluents significantly alters the behavior of the material under confinement and decreases the suppression in \( T_g \) under confinement. Very recently, Evans et al.\(^\text{5}\) have shown that there also exists a one-to-one correlation between the bulk state fragility of the material and \( T_g \)-nanoconfinement effects. However, the universality of this correlation remains unsettled.

In our simulations, we have seen that this universality does not hold well across all the systems in which bulk state fragility is tuned via multiple routes – by changing bond length of the neat polymer and by employing small molecule and oligomer diluents.

With the requirement of more mechanically robust and flexible materials for applications like flexible electronic displays, organic solar cells etc., we require deeper understanding of the effect of confining materials on the properties of these
nanostructured materials. Nanoconfinement effects, such as changes in glass transition temperature\textsuperscript{19–25}, elastic modulus\textsuperscript{26,27}, and other transport properties\textsuperscript{28}, as compared to the bulk properties of the material, have most commonly been attributed to the presence of long-ranged gradients in dynamics and $T_g$ reported in the vicinity of interfaces in these materials\textsuperscript{29–39}. This would appear to represent a finding of extreme scientific and technological relevance, as it has been suggested that these shifts provide a window into underlying scales of cooperative dynamics in supercooled liquids\textsuperscript{14,15,19,23,31,32,35–38,40–43}, and they are implicated in determining material properties in various applications as mentioned before.

However, this conclusion has been complicated by work reporting that $T_g$, when measured by dynamic methods such as dielectric spectroscopy\textsuperscript{44}, as opposed to measurements from ellipsometry and calorimetry\textsuperscript{45–48}, frequently exhibits much weaker shifts under nanoconfinement. This discrepancy has raised questions of whether nanoconfinement and interfaces indeed impose long-ranged alterations in the dynamics of glass-forming liquids. Attempts to explain this have included suggestions of inadequate film annealing\textsuperscript{49}, solvent contamination\textsuperscript{50}, differences in effective timescale\textsuperscript{50,51}, flaws in data analysis, and the proposition that the pseudo-thermodynamic $T_g$ is entirely decoupled from underlying dynamics under nanoconfinement due to free volume diffusion effects\textsuperscript{46}. Previously, researchers have shown that there exists discrepancies in the behavior of nanoconfined materials when they are probed by different metrologies. For example, nanoconfinement effects as probed by ellipsometry and incoherent neutron scattering do not agree with each other, and researchers have concluded that this discrepancy can be explained if we consider the sensitivity of different experimental techniques to the
distribution of dynamics in the film. In this light, it is very important for us to understand the significance of weighting factor when measuring dynamics using different probes.

One of the applications of modifying the interface of a material is seen in the emergence of a new class of glassy materials – “ultrastable” glasses, produced by vapor deposition. These materials have emerged over the past several years and exhibit unusual kinetic and thermodynamic stability, with enhanced densities, enhanced moduli, suppressed energies, and increased softening temperatures. Estimates suggest that these enhancements would require tens to thousands of years to obtain via a typical temperature quench into the glass state. Due to these extraordinary properties and speculation that they may closely approach a posited “ideal glass” state, these materials have been the focus of great attention. Although widely studied, the precise mechanism behind the emergence of exceptional mechanical properties in this class of materials is not clearly understood.

Based on the above viewpoints we developed about diluents and dynamic interfaces, we intend to do the following in this study.

1. In Chapter IV, we look at the design principles guiding the design of newer diluents which enable controlled and targeted alterations in a polymer’s glass transition and associated mechanical properties. We also look at the bounds on the alterations in these properties achievable via introduction of diluents and attempt to answer if these effects can be understood and predicted via generalized entropy theory of glass formation.

2. In chapter V, we detail the impact of measuring $T_g$ via dynamic and pseudo-thermodynamic approaches in polymer thin films. We propose suitable weighting factors to account for the discrepancies arising from these methods of measurement.
3. In chapter VI, we delve into understanding the impact of bulk state behavior of the material on the observed $T_g$-nanoconfinement behavior. We look at the one-to-one correlation between bulk state fragility and $T_g$-nanoconfinement as previously suggested by researchers\textsuperscript{5}. We enumerate all the confounding variables that effect the nanoconfinement behavior of the material.

4. Lastly, in Chapter VII, we list the open questions present in understanding the exceptional properties of ultrastable glasses and provide insights to better understand the behavior of “ultrastable” glasses.
CHAPTER II
BACKGROUND AND LITERATURE REVIEW

This chapter presents a review of different classes of polymer diluents and their applications reported in the literature. Several classification schemes are discussed, analyzed and we have proposed the requirement of a better classification scheme, which is a major component of the thesis. This also includes the current classification of diluents and showcases the new classifications scheme we are proposing to classify diluents. In addition, this chapter presents detailed overview of the existing literature on the physics of nanostructured materials and presents the current understanding and further research scope of the behavior of nanostructured polymers.

2.1 Overview

Introduction of a molecular diluent – a low-volume-fraction molecular additive – is one of the most commonly employed methods of modifying a polymer’s properties. When added in low volume fractions, they start influencing polymer properties, including the glass formation behavior, mechanical response, and transport properties of the host polymer matrix. For this reason, extensive research efforts over more than a half-century have attempted to guide the selection of additives with targeted effects on selected polymers. Since at least the 1960s, diluents have generally been divided into two classes: plasticizers and antiplasticizers\textsuperscript{10,11}, the precise definitions of which have varied over time
and between research groups. The former class is fairly universally defined as comprising
diluents that simultaneously soften a polymer in the glassy state and reduce its glass
transition temperature $T_g^{57-59}$. In practice, the term “antiplasticizer” has often been
employed as a ‘catch-all’ to describe any additive that does not neatly fit into the above
category; however, it most commonly and recently refers to additives that suppress a
polymer’s $T_g$ yet enhance its glassy modulus, typically below a critical ‘antiplasticization’
onset temperature$^{1,2,60-65}$. These molecular diluents are scientifically and commercially
critical tools for control of glass formation behavior and mechanical properties; they are
employed in applications including structural and commodity polymers, foods and food
preservation$^{66-71}$, preservation of protein-based pharmaceuticals$^{72-74}$, separations$^{60,75-77}$,
barrier films$^{78}$, nanostructured polymers for use in microelectronics$^{79}$, and fundamental
studies on the physics of glass formation$^{1,4,65}$.

However, a review of this literature, combined with recent theoretical predictions$^2$,
suggests that diluent effects on polymers are far richer than accounted for by this binary
classification scheme, offering the possibility of a diverse range of effects on the low- and
high-frequency dynamics and mechanics of polymers. These insights suggest that these
‘old’ tools have the potential to offer a new set of strategies for rational design of polymeric
materials with improved properties and performance. More effective use of diluents to this
end will require a modernized and more physics-based understanding of the nature of their
effects on host polymers and the dependence of these effects on diluent and polymer
molecular properties. Here we synthesize recent insights into diluent physics and glass
formation behavior more generally to establish a new classification framework enabling
quantification of this broader range of diluents’ effects. Application of this framework to
systems characterized in the literature confirms the existence of a range of diluent/polymer effects offering a high degree of control of polymer properties. From our simulations, we also indicate the possibility of several apparently undiscovered classes of diluent that would be of considerable value in polymer design. Several recent theoretical frameworks offer the potential to aid in design and discovery of these additives, and we highlight a critical need for improved structure-property relations in support of this goal. This new synthesis of the literature identifies a renewed effort in diluent science as a key need and opportunity in ongoing efforts to achieve more rational control of the properties of polymers and other soft materials.

In light of this understanding, we would like to address the following three major challenges in the understanding of polymer/diluent blends

1: Diluent characterization and classification

A review of the literature indicates that diluent effects on polymer linear-regime dynamics and mechanics are far more diverse than can be captured by the binary plasticizer/antiplasticizer classification scheme. How can the classification of diluents be modified to more completely capture the diversity of these effects while remaining both tractable and mechanistically meaningful?

2: Diluent structure-property relations

The overall goal of the use of molecular diluents in polymers is to more rationally obtain targeted polymer properties without dramatic alterations to polymer chemistry. Accomplishing this goal requires an answer to the following question: how does a diluent’s molecular structure determine its impact on the host polymer?
3: Interrelations between diluent effects on low- and high-frequency dynamics

Diluents can have dramatically different effects on a polymer’s high-frequency and low-frequency dynamics. Is there any relationship between a given diluent’s effects on these two ranges of dynamics that would constrain the property modifications that can be achieved with diluents, or are they genuinely unrelated?

The following three sections synthesize the extant literature into a current ‘state of the art’ perspective on each of these challenges. Discussion is restricted to the impact of diluents on polymer linear-regime dynamics and mechanics. We put off to a later time any discussion of the many effects of diluents on nonlinear mechanical response such as polymer toughness, since in our view an understanding of these effects must await a more complete understanding of linear-regime phenomena in polymer/diluent blends.

2.2 Diluent characterization and classification

In this section, we present an overview of all the existing understanding of classification of polymer diluents.

2.2.1 The current understanding: phenomenology of diluent effects on low- and high-frequency dynamics

The large body of literature on diluent/polymer blends suggests a dizzying array of linear-regime polymer properties that can be altered by diluent introduction. These include at least viscosity ($\eta$), segmental $\alpha$-relaxation time, the timescales of higher-frequency relaxations such as the dielectric beta, modulus, Debye-Waller factor, and permeability. The usual classification of these additives into plasticizers and antiplasticizers can be understood both as a convenience and a historical artifact: the
earliest-studied additives tended to suppress both the glass transition temperature $T_g$ and the glassy modulus and were accordingly dubbed plasticizers\textsuperscript{57,58}. It is intuitively sensible that these effects should be accompanied by an enhancement in permeability and free volume and a suppression in viscosity and segmental relaxation times, and additives observed to accord with this pattern are generally classified as plasticizers. Beginning in the 1960s with the seminal work of Jackson and Caldwell\textsuperscript{10,11}, it became apparent that certain diluents do not fit this pattern, most commonly by inducing an enhancement in glassy modulus over at least some temperature range. Jackson and Caldwell dubbed such additives antiplasticizers, and this term has since been employed to describe diluents with effects differing from those of plasticizers in various ways, including either enhancement of the glassy modulus\textsuperscript{10,75,81} or enhancement of $T_g$\textsuperscript{12}. As stated in the previous section, the literature has generally converged on use of this term to describe diluents that, like plasticizers, suppress $T_g$, yet enhance the glassy modulus, commonly below an onset temperature denoted $T_{anti}$\textsuperscript{1,2,60–65}.

The observation that a diluent-induced suppression in $T_g$ can be accompanied by either a suppression or enhancement in the glassy modulus indicates that molecular diluents can in general induce distinct and even opposing alterations in low- and high-frequency ranges of polymer dynamics\textsuperscript{83,85}. Furthermore, it is clear that diluents’ effects on each frequency range can be highly temperature dependent, sometimes exhibiting shifts from enhancement to suppression of dynamics on heating or cooling\textsuperscript{1–3,6,15,86}. For this reason, recent work has emphasized the importance of characterizing temperature-dependent effects of a given diluent on both high- and low-frequency ranges of polymer relaxation\textsuperscript{7}. This constitutes an important departure from earlier work, which often employed a

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narrower characterization approach focused on, for example, the diluent-induced shift in modulus at a single temperature and the diluent-induced shift in $T_g$. The current understanding of the overall phenomenology of diluent effects on low- and high-frequency linear regime dynamics is as follows.

Molecular diluents’ effects on polymer low-frequency relaxation behavior is generally quantified by changes in the structural relaxation time $\tau_\alpha$, which characterizes the low-frequency relaxation process most closely associated with $T_g$ itself (by a common convention, $T_g$ is defined as the temperature at which $\tau_\alpha = 10^2$ or $10^3$ s)$^{87}$. Shifts in $\tau_\alpha$ also tend to be reflected in the viscosity $\eta$, although in polymers the temperature dependence of these quantities can become somewhat decoupled near $T_g$, most commonly with $\eta$ exhibiting a weaker temperature dependence than $\tau_\alpha$.$^{88}$ Whereas much prior work in the field has focused on quantification of diluent-induced shifts in $T_g$, evidence indicates that a full accounting of alterations in low-frequency dynamics requires of changes in the temperature dependence of $\tau_\alpha$. This temperature dependence is commonly quantified based on the “fragility” of glass formation, which, taken together with $T_g$, characterizes the strength of the temperature dependence of structural relaxation dynamics upon cooling through $T_g$.$^{88,89}$ Specifically, fragility is often quantified by the “kinetic fragility index” $m$

$$m \equiv \frac{\partial \log \tau}{\partial T_g / T} \bigg|_{T=T_g}$$

which is the slope of $\tau_a$ on an Arrhenius plot at $T_g$, normalized by $T_g$. $m$ has a minimum value in the range of 16 for perfectly Arrhenius glass-formers (SiO$_2$ being the typical example of a ‘non-fragile’ glass-former). While it has no known theoretical upper bound,
$m$ is in the range of 200 for the most fragile glass-formers known (polyvinylchloride and polyetherimide)\textsuperscript{90}. Experimental\textsuperscript{6,10,63,64,68,91,92}, theoretical\textsuperscript{2}, and computational\textsuperscript{1,3,65} evidence suggest that both traditional plasticizers and antiplasticizers, in addition to suppressing $T_g$, most commonly reduce the fragility of glass formation, effectively broadening the range of temperatures over which $\tau_\alpha$ grows upon cooling towards $T_g$ (Figure 2.1).

Diluents additionally can alter polymers’ high frequency dynamics, as reflected in a range of properties including the dielectric Johari-Goldstein relaxation process\textsuperscript{6,7,93}, the strength of the fast beta relaxation process as reflected in the Debye-Waller factor $<u^2>$\textsuperscript{72,94}, and other loss transitions at higher frequency than the $\alpha$-relaxation process. Since

Figure 2.1: (Left) Plot showing the super-Arrhenius behavior of fragile liquids and Arrhenius behavior of strong liquids. (Right) Plot showing changes in fragility of a pure polymer when a small molecule diluent is introduced in low concentrations. Red circles show the impact of fullerene on polyamide, data replotted from reference\textsuperscript{104}. Blue triangles show the impact of fullerene on polystyrene, data replotted from reference\textsuperscript{85}. 
polymers’ glassy moduli are primarily a measure of the cumulative magnitude of these high-frequency processes, glassy modulus also tends to track with these measures of high-frequency dynamics, with weaker high-frequency relaxations correlating with a higher glassy modulus. Glass-state permeability also often trends with these high frequency properties, with stronger relaxation often corresponding to greater permeability.

As with their effect on low-frequency relaxation, it has long been known that diluents’ effects on high-frequency dynamics and modulus can be strongly temperature dependent. For example, as noted above, antiplasticizers commonly induce a crossover from enhancement to suppression of high frequency dynamics (or suppression to enhancement of modulus) upon cooling through a temperature known as the “antiplasticization” temperature. The introduction of glycerol to trehalose is a canonical example of this effect. However, the opposite trend in temperature has also been observed, for example in the introduction of Aroclor to polycarbonate, and in many cases, where studies have focused on a single temperature, inadequate data is available to characterize this trend.

Recently, Pasurek et al. have suggested a scheme for classification of these effects based upon quantification of changes in the timescale $\tau_\beta$ of the Johari-Goldstein dielectric beta relaxation process. Specifically, because this process tends to exhibit a highly Arrhenius temperature dependence, especially at temperatures below $T_g$, it is possible to quantify a diluent’s effects on $\tau_\beta$ based on changes in the apparent activation enthalpy $H_a$ and entropy $S_a$ of activation for this process based on the free energy activation model expressed by the equation
\[
\ln \tau_\beta = \ln \tau_0 + \frac{G_a}{kT} = \ln \tau_0 - \frac{S_a}{k} + \frac{H_a}{kT} \quad 2.2
\]

where \( G_a \) is the activation free energy, \( \tau_0 \) is the high-temperature limit of relaxation time (which is fairly fixed in the range of 10fs – 100fs for nearly all systems), and where \( S_a \) and \( H_a \) can be determined from the intercept and slope of a plot of \( \ln(\tau_\beta) \) vs \( 1/T \). On the basis of shifts in these two quantities upon introduction of a diluent, Psurek et al\(^7\) proposed ten categories of diluent effects on high frequency dynamics alone. These categories specifically reflected the sign of the change in \( \tau_\beta \), the presence or absence of an antiplasticization onset temperature, and its location relative to the temperature range of interest.

Broadly speaking, these observations indicate that characterizing the full temperature dependent effect of a diluent on both high- and low-frequency dynamics requires, at a minimum, quantification of the changes in four quantities: \( T_g \), the fragility of glass formation \( m \), and a local activation enthalpy \( E_a \) and entropy \( S_a \) for a fast, local relaxation process. Since this fact has been unrecognized through most of the history of the study of diluents, many of the large number of diluents previously described as falling into a single category (e.g. plasticizers) may in fact differ in important ways in their effects on one or more of these properties.

Indeed, the recognition of this minimal characterization scheme suggests that no binary (plasticizer/antiplasticizer) classification scheme will likely be sufficient to fully describe a given additive’s effects on linear-regime segmental dynamics. As an example, consider the following three polymer/diluent pairings: trehalose/glycerol, PC/Aroclor, and nylon/poly(aniline). Relative to the pure polymer, the first of these exhibits suppressed \( T_g \),
enhanced stiffness at low temperature, and suppressed stiffness at high temperature. The second exhibits suppressed $T_g$, suppressed stiffness at low temperature, and enhanced stiffness at high temperature. The third exhibits enhanced $T_g$. It is clear that these cannot be meaningfully described by any pair of categories. On the other hand, the classification scheme of Psurek et al., if extended to include low-frequency dynamics, would seem to lead to at least 40 classes of diluent – 10 for high-frequency dynamics multiplied by 4 to account for possible combinations of shifts in $T_g$ and $m$ – presenting a somewhat daunting categorization space. Accordingly, in the following section we propose a new minimal framework for classification of diluent effects on linear-regime segmental dynamics that captures practical distinctions between diluents while retaining physical insight.

2.2.2 Proposed diluent classification framework

Inspired by the recent progress described above, we propose a tractable framework for the classification of diluents, aiming to guide materials design as well as provide physical insight into the molecular mechanisms underlying diluent effects on segmental dynamics. We begin with the proposition that such a framework must incorporate the temperature dependence of diluent-induced alterations in dynamics. In particular, we focus on the presence or absence of a crossover temperature where the diluent’s effect switches from suppression to enhancement of a given relaxation process. We note that this framework does not attempt to capture the effect of concentration on diluent effects; previous studies have indicated that many additives, regardless of their low-concentration effect, revert to suppression of the high frequency modulus (plasticization) at elevated concentration. While it is certainly possible that this is not a general result, we reserve consideration of this issue to a future study.
In order to classify diluent effects on high frequency relaxation, we begin with the approach of Psurek et al. described in the introduction and reflected mathematically by equation 2.2. Specifically, assuming that alterations in $\tau_0$ can be neglected given its fairly universal value, the change in the beta relaxation time with introduction of an additive is

$$\ln \frac{\tau_\beta^a}{\tau_\beta^I} = \frac{-\Delta S_a}{k} + \frac{\Delta H_a}{kT}$$

Where $\Delta S_a = S_a^H - S_a^I$ and $\Delta H_a = H_a^H - H_a^I$ are the change in activation entropy and enthalpy of this high frequency process, respectively, upon addition of a diluent, and superscripts II and I denote the adulterated and pure polymers, respectively. In an effort to simplify the 10-category framework suggested by Psurek et al. on this basis, we establish a classification framework based purely on the question of whether a crossover in $\tau_\beta$ between the pure and adulterated systems exists, and, if so, on the direction of the crossover. We specifically choose the range temperature range $0 < T < T_g$ because a modulus, distinct beta relaxation process, and other distinct high-frequency processes generally emerge upon cooling through a temperature modestly above $T_g$ and are most pronounced below $T_g$ itself. For many of these processes, the onset temperature for these features is a crossover temperature $T_c$ that is generally found in the range of 1.15 to 1.4 $T_g$. We note that employing $T_c$ rather than $T_g$ as the upper limit to this range would not qualitatively alter the classification scheme but could shift some individual systems near the bounds of categories one way or the other.

Beginning with equation 2.3, the crossover point between the pure and adulterated polymer is given by the expression
The range in which a relevant crossover is found is then given approximately by the pair of inequalities

\[ 0 < \frac{\Delta H_a / k T_g^{\text{pure}}}{\Delta S_a / k} < 1 \]  \hspace{1cm} 2.5

On this basis, a given concentration of a particular polymer/diluent blend will occupy a single point in a plot of $\Delta S_a / k$ vs $\Delta H_a / k T_g^{\text{pure}}$, with the location of this point relative to the range specified above indicating whether $\tau_\beta$ is increased at all temperatures, decreased at all temperatures, or exhibits a crossover from suppression to enhancement on heating or vice-versa. Figure 2.2 depicts such a plot for PC diluted with several concentrations of Aroclor.\textsuperscript{7} This figure serves as a dynamic classification diagram for the effects of Aroclor on PC high frequency dynamics – the region occupied by the system determines the class of the diluent’s effect and the antiplasticization temperature, if present, can be extracted from the figure via equation 2.4.

This approach has a major shortcoming: in some polymeric materials, notably many simulated polymers and experimental polymers that are not amenable to dielectric spectroscopy, the Johari-Goldstein beta relaxation process is absent or not detectable. In order to extend this classification framework to such systems, we note that a number of studies have identified a phenomenological correspondence between additive-induced shifts in $\tau_\beta$ and additive-induced shifts in the Debye-Waller factor $\langle u^2 \rangle$.\textsuperscript{7,73} The Debye-Waller factor is a measure of local segmental rattle space, on a picosecond timescale, that
is experimentally measurable via Neutron scattering, Mossbauer scattering, and time-resolved Stokes shift experiments and is easily obtained in molecular simulations. It appears to be a fairly general observation that additive-induced reductions in $\tau_\beta$ are mirrored by enhancement of $\langle u^2 \rangle$ and vice versa, although the origin of this relationship has remained unclear. Here we propose a simple scaling model for the relationship between these quantities that permits construction of a ‘high-frequency dynamics diagram’ comparable to Figure 2.2 from $\langle u^2 \rangle$ data.

We begin with the proposition of Hall and Wolynes that the rattle space $\langle u^2 \rangle$ is directly related to the free energy of activation of the alpha relaxation process as
where $u_0$ is interpreted as a critical average distance a particle must travel for activation to occur. As reviewed by Dyre, the relationship given by equation 2.6 can generally be interpreted in terms of an elastic activation model of supercooled liquid dynamics, where $kT/\langle u^2 \rangle$ measures the strength of a local effective elastic confining potential within a harmonic approximation for the form of this potential\textsuperscript{99}. We note that recent work has indicated that this form provides, at best, a rough leading order description of the dynamics of glass-forming liquids, and several studies have proposed modifications that lead to an improved description of experimental and simulation data\textsuperscript{4,100,101}. We propose, however, that equation 2.6, if reapplied to the $\beta$-relaxation rather than $\alpha$-relaxation process, provides an excellent leading-order basis for understanding the apparent relationship between $\tau_\beta$ and $\langle u^2 \rangle$. Specifically, within the ‘elastic activation’ view promoted by Dyre and others, it is reasonable to expect that even a local activated process such as the beta relaxation should be gated by an effective local elasticity of the medium. It is well-established that the high-frequency modulus of a material scales with the quantity $kT/\langle u^2 \rangle$, such that the essential view described above should hold for $\tau_\beta$. Moreover, since the $\beta$-relaxation process exhibits a very nearly Arrhenius temperature dependence, rather than the super-Arrhenius dependence of the $\alpha$-relaxation, it is more likely that the relatively simple relationship given by equation 2.6 should quantitatively describe this process.

Beginning with this proposition, equation 2.6 leads to the relationship

\[
\frac{kT}{\langle u^2 \rangle} = \frac{H_\beta}{u_0^2} - \frac{S_\beta}{u_0^2} T \equiv \hat{H}_\alpha - \hat{S}_\alpha T
\]
where \( H_a \) and \( S_a \) are proposed to correspond to leading order to the activation enthalpy and entropy introduced in equation 2.2 for the beta process. Notably, this relationship, combined with the Arrhenius temperature dependence of \( \tau_\beta \), would require \( kT/\langle u^2 \rangle \) to exhibit a linear temperature dependence below \( T_g \), and this is indeed consistent with the results of prior work\(^\text{94}\). On this basis, a fit to sub-\( T_g \) data for \( kT/\langle u^2 \rangle \) data should yield \( \hat{H}_a \) and \( \hat{S}_a \) from its intercept and slope, respectively. Under the assumption that \( u_0^2 \) varies at most weakly with the addition of an additive, changes in these two values upon addition of a diluent can be attributed to shifts in \( H_a \) and \( S_a \) and can therefore be employed to construct plots comparable to Figure 2.2. Specifically, the regime in which a crossing is found can be defined as

\[
0 < \frac{\Delta H_a / k T_g^{\text{pure}}}{\Delta S_a / k} < 1
\]

We employ a similar approach as that above to categorize diluent effects on \( \tau_\alpha \) based on the nature of crossovers in diluent-induced alteration in \( \tau_\alpha \). Specifically, we employ a Vogel-Fulcher-Tammann fitting form to describe the temperature dependence of \( \tau_\alpha \) in the pure and adulterated systems:

\[
\ln \tau_\alpha^i = \ln \tau_0 + \frac{D_i^i T_0^i}{T - T_0^i}
\]

where \( T_0 \) is an extrapolated divergence temperature, \( I/D \) is related to the fragility of glass formation, \( \tau_0 \) is the high-temperature relaxation time, and the superscript “\( i \)” is \( I \) for the pure system and \( II \) for the adulterated system. We note that this is not a unique choice of fitting form, an alternate use of, for example, the double-exponential fitting form recently
proposed by Mauro et al. for the temperature dependence of $\tau_\alpha$ is not expected to qualitatively alter this approach.

Beginning again with the assumption that changes in $\tau_0$ can be neglected, the intersection between the VFT relations for the pure and adulterated polymer is given by:

$$\frac{T_{cross}}{T_0^I} = \frac{D^I/D^\mu - 1}{(D^I/D^\mu)(T_0^I/T_0^\mu) - 1}$$  \hspace{1cm} 2.10

Equation 2.10 could be employed directly to produce a figure similar to Figure 2.2 but for the alpha-relaxation process. However, the polymer glass transition is more commonly characterized in terms of $T_g$ and fragility of glass formation than in terms of VFT parameters. In order to recast equation 2.11 in terms of $T_g$ and fragility rather than $T_0$ and $D$, we make use of the relation

$$T_g = DT_0^\tau + T_0$$  \hspace{1cm} 2.12

which is simply the VFT relation at $T = T_g$, where $\tau_g$ is defined as $\tau_\alpha$ at the temperature $T = T_g$. Employing this equation and substituting the VFT relation into equation 2.1 definition of $m$ yields the equation

$$m = \log \frac{\tau_g}{\tau_0} \left[1 + \frac{T_0}{T_g} \left(1 - T_0/T_g \right) \right]$$  \hspace{1cm} 2.13

Rearranging equation 2.13 yields

$$T_0 = T_g M$$  \hspace{1cm} 2.14
where \( M \), which we refer to as the “degree of fragility”, is given by

\[
M = \frac{m/m_A - 1}{m/m_A + 1} = \frac{E_a - E^A_a}{E_a + E^A_a} = \frac{T_0}{T_g}
\]

where \( m_A = \log \left( \tau_g / \tau_0 \right) = 16 \) is the fragility of a perfectly Arrhenius glass-forming liquid and \( E^A_a = kT_g \ln \left( \tau_g / \tau_0 \right) \) is the activation energy that would be required for a perfectly Arrhenius glass-forming liquid to have the same dynamic \( T_g \) as the system under consideration.

The new measure of fragility provided by equation 2.15 offers several advantages over the more conventional kinetic fragility index \( m \). First, whereas values of \( m \) can range from 16 to infinity, \( M \) is strictly bounded from 0 to 1, with \( M = 0 \) indicating a perfectly Arrhenius glass former and \( M = 1 \) indicating a hypothetical completely ‘abrupt’ glass
transition. This feature is apparent in Figure 2.3, which shows a mapping of \( m \) to \( M \) for several representative polymeric and nonpolymeric glass-formers. Conceptually, whereas the value of \( m \) includes an Arrhenius component, \( M \) directly quantifies the strength of deviation from an Arrhenius temperature dependence. \( M \) also is equal to the ratio of the characteristic temperatures \( T_0 \) and \( T_g \), consistent with prior work suggesting that ratios of such characteristic temperatures of glass formation provide a measure of fragility\(^{1,103}\).

Use of equations 2.12 and 2.14 in equation 2.10 yields

\[
\frac{T_{\text{cross}}}{T_{g,\text{pure}}} = \left(1 - \frac{1}{1-M_{\text{pure}}^{M}}\right)^{-1}
\]

Equation 2.16 indicates that the location of the crossover temperature in \( \tau_a \) depends on the relative \( T_g \)'s of the pure and adulterated polymers, the diluent-induced change in \( M \), and \( M \) for the pure polymer. In general a crossover in \( \tau_a \) will exist when \( T_{\text{cross}} > T_{g,\text{pure}} \), \( T_{\text{cross}} > T_g \), and \( T_{\text{cross}} < T_{\text{max}} \). \( T_{\text{max}} \) sets the upper temperature below which a crossover in \( \tau_a \) is of interest; this may be the onset temperature for degradation \( T_D \) or the high-temperature onset of glass formation \( T_A \), for example. As shown by Figure 2.4, this leads to a dynamic classification diagram for diluent effects on polymer low-frequency dynamics that is analogous to that offered by Figure 2.2 for diluent effects on high-frequency dynamics. Specifically, within a plot of \( (M - M_{\text{pure}})/(1 - M_{\text{pure}}) \) vs. \( 1 - (T_{g,\text{pure}}/T_g) \), each system is represented as a single point, and the regions bounded by the inequality
\[
\frac{T_{\text{cross}}}{T_{g,\text{pure}}} < \left(1 - \frac{T_{g,\text{pure}}}{T_g} \right)^{-1} \left(1 - \frac{M - M_{\text{pure}}}{1 - M_{\text{pure}}} \right)
\]

and by the vertical axis \(1 - \frac{T_{g,\text{pure}}}{T_g} = 0\) denote regions in which a crossover exists.

Within this framework, the impact of a diluent on a given host polymer is specified based on its location in one figure showing \(\Delta H_a/kT_{g,\text{pure}}\) vs \(\Delta S_a/k\) (such as Figure 2.2) and one showing \(\frac{(M - M_{\text{pure}})}{(1 - M_{\text{pure}})}\) vs. \(1 - \frac{T_{g,\text{pure}}}{T_g}\) (such as Figure 2.4). The diluent/polymer pair may be classified based on their region in these two figures, specifying the sign of their effect on the beta and alpha relaxation times at low and high temperature, effectively. For example, the blend of 15% Aroclor in PC discussed above can be classified graphically as

\[
\begin{array}{c}
\text{low } T \\
\tau_\alpha \\
\downarrow
\end{array}
\begin{array}{c}
\text{high } T \\
\tau_\beta \\
\uparrow
\end{array}
\]

or in shorthand as \(\downarrow \uparrow\) or \(\downarrow \uparrow \uparrow \uparrow\). This leads to a total of 16 possible diluent classes differing in their impact on a host polymer’s low- and high-frequency segmental dynamics.

Based on the standard definitions of ‘classical’ plasticizers and antiplasticizers, supplemented by predictions of the Generalized Entropy Theory (GET) for the most common impact of these classes on fragility of glass formation\(^2\), Figure 2.2 and Figure 2.4 additionally show how these traditional categories fall into the proposed classification scheme.
In Figure 2.5, we extract data from prior work in understanding the effect of fullerene loading on polyamide (PA)\textsuperscript{104} and polystyrene (PS)\textsuperscript{85}. We see a drastically different behavior of the additive in the PA matrix as compared to being mixed with PS. Depending on the additive polymer interactions, fullerene tends to lower the $T_g$ of PA at all concentrations and its effect on fragility is concentration dependent. On the other hand, fullerene when mixed with PS, tends to enhance $T_g$ and fragility of the system at the concentration studied. The key question is now whether all of these theoretical categories correspond to some real-world system. If so, what set of diluent molecular properties lead to each category? Alternatively, does some relationship exist between diluent effects on

\[ \frac{M-M_{\text{pure}}}{M_{\text{pure}}} \] \[ \frac{1-(T_{g,\text{pure}}/T_g)}{1-(T_{g,\text{pure}}/T_g)} \]

Figure 2.4: Dynamic classification diagram for diluent effects on low frequency dynamics. The circle, square, triangle, and diamond denote the behavior of PC-Aroclor blends at 0.2, 0.15, 0.1 and 0.05 Aroclor weight fraction, respectively, based on reanalysis of literature data in reference\textsuperscript{7}. AP and P indicate the regions occupied by classical antiplasticizers and plasticizers, respectively. Each region is labeled by a pair of arrows indicating the effect on the associated property ($\tau_\alpha$) at low (left arrow) and high (right arrow) temperature.
high- and low-frequency dynamics that would prohibit some of the above 16 combined categories?

Figure 2.5: Dynamic classification diagram for diluent effects on low frequency dynamics. Solid circle, square, and triangle denote the behavior of PA-fullerene blends at 0.02, 0.04, and 0.08 weight percent of fullerene loading, respectively, based on reanalysis of literature data from reference 104. Hollow circle, square, and triangle denote the behavior of PS-fullerene blends at 0.6, 1, and 2 weight percent of fullerene loading, respectively, based on reanalysis of literature data from reference 85.

2.3 Structure-property relationships for polymer/diluent blends

In this section, we present an overview of the existing theories predicting structure property relationships for polymer/diluent systems.

2.3.1 Generalized entropy theory

Dudowicz et.al. 105 postulated the Entropy theory of glass formation which indicates that change in fragility due to change in local packing efficiency. One way to change packing efficiency is to add small molecule diluents which tend to increase packing efficiency in the glass state and enhances the ability of a polymer melt to form a glass 15, 106, 107. This indicates a decrease in fragility. Now, addition of small molecule
diluents not only affects fragility but also causes changes in local stiffness, compressibility and mobility of a polymer\textsuperscript{2,65,108}. It has been argued that changes in fragility are related to changes in Debye-Waller factor, $\langle u^2 \rangle$, which in turn is related to efficiency of local packing\textsuperscript{103,108}. $\langle u^2 \rangle$ is the measure of the amplitude of vibrations of a particle in a cage and the inverse of $\langle u^2 \rangle$ is a rough measure of local stiffness. So it is expected that changes in fragility scale with changes in $\langle u^2 \rangle$\textsuperscript{1,15,108}. Entropy theory of glass formation predicts that changes in properties of glass forming liquids can be induced by film confinement or addition of diluents. It also predicts various trends in variation in fragility with change in chain stiffness, cohesive energy and chain length\textsuperscript{103,109}. Fragility (and packing efficiency) can be tuned by changing molecular properties, changing composition of additive, and by changing molecular properties of additives.

Decrease in size of the diluent causes a larger depression in $T_g$ and renders the antiplasticized system a strong glass former (decrease in fragility) compared to pure polymer\textsuperscript{2}. But this decrease in size does not show significant effect on isothermal compressibility ($\kappa$) and packing efficiency\textsuperscript{2} (density, $\rho$). For a fixed size of the diluent, it is observed that depression in $T_g$, with respect to pure polymer, decreases with increase in cohesive energy\textsuperscript{2}. On the other hand this increase in cohesive energy makes the mixture a stronger glass former\textsuperscript{1}. A plot of isothermal compressibility suggests that a transition from plasticization to antiplasticization occurs by increasing the cohesive energy of the additive\textsuperscript{1}. But care should be taken in specifying the temperature range considered as antiplasticization-plasticization transition occurs by varying temperature\textsuperscript{7,108} (as seen in section above). Suppression in $\beta$-relaxation time has been observed as a consequence of decrease in isothermal compressibility\textsuperscript{110}. Thus additives which are smaller in size
compared to the statistical segment length of polymer and have *weak* attractive interactions are good glass plasticizers\(^2\,\text{111}\). On the other hand, additives which have *strong* attractive interactions are good glass antiplasticizers\(^2\). As the stiffness of diluent increases, we see a decrease in depression in \(T_g\)\(^2\). Generally this is observed with diluents of high molar mass as they have higher stiffness\(^2\).

2.4 Interrelations between effects on high- and low-frequency dynamics

Moving forward, it is very important for us to understand how the high- and low-frequency properties can be predicted and then ask the question as to how these quantities are related. In an effort to do this, we present here the past and existing theories to predict the glass formation behavior in a polymer and summarize the generalized localization model which predicts the interrelations between high- and low-frequency dynamics.

2.4.1 Free volume theory

For decades, the concept of free volume has been used to quantify and explain the changes in the dynamical and mechanical properties of polymers. Many glass formers, including polymers, tend to exhibit super-Arrhenius behavior and the focus of the developing theories was to understand this behavior. The basic form of Arrhenius behavior is given by the Andrade equation\(^\text{112}\), given by equation 2.18.

\[
\ln \eta = \ln A + B / T
\]

2.18

In his seminal work\(^\text{113}\), Doolittle replaced \(T\) in equation 2.18 with relative free volume to obtain equation 2.19

\[
\ln \eta = \ln A + B \left(\frac{v_0}{v_f}\right)
\]

2.19
where, \( \eta \) is the coefficient of viscosity, \( v_0/v_f \) is the relative free volume, and \( A \) and \( B \) are constants for a given material. A simple Arrhenius form, as in equation 2.18, does not capture the temperature dependent behavior of most of the glass-formers, but the form predicted by Doolittle, which includes a complicated temperature dependence, led him to predict better temperature dependence in simple alkanes (\( n \)-heptadecane). The fundamental problem arising here is to accurately measure the free volume of the systems from experiments.

The super-Arrhenius behavior in many glass formers lies in accurately predicting \( B \) (apparent activation energy), which increases with decrease in temperature. Vogel-Fulcher-Tammann\(^{114-116}\) (VFT) came up with equation 2.20

\[
\ln \eta = \ln A + B / (T - T_0)
\]

which accurately tracks with experimentally observed behavior in glass forming materials with relatively better success. This eliminates any formal measure of free volume and \( A \) and \( B \) parameters can be obtained from tracking the viscosity dependence on temperature.

Recently Jane Lipson and co-workers\(^{117,118}\) have taken the free volume approach to a further level by defining free volume to be the difference between volume of the sample and hard core volume. They define hard core volume to be the product of number of molecules (\( N \)), number of segments per molecule (\( r \)) and the temperature independent hard core volume per segment (\( v \)). This approach is advantageous as these quantities are easily quantifiable. Also, hard core volume remains fixed with changes in temperature or pressure. This effectively gives us the amount of free space left in the system. The earlier
approaches of free volume present a very ambiguous definition of free volume\textsuperscript{119–122} and all that has been clarified by this definition of free volume in the locally correlated lattice (LCL) model from Jane Lipson and co-workers. They found a very strong correlation between the percent free volume and \( T_g \), without any prior assumptions between the free volume and \( T_g \).

2.4.2 Elastic activation theories

There are many theoretical approaches to predict the slow dynamics of glass-forming materials. One of the kinetic approaches is idealized mode coupling theory (IMCT)\textsuperscript{123,124}. This provides a self-consistent description of the local dynamics of the material occurring due to caging. This theory predicts the non-ergodic behavior of glass forming materials. Although this theory has been formulated for fluids comprised of spherical particles, there has been a lot of literature extending this framework to unentangled bead-spring polymers\textsuperscript{125} and other non-spherical molecular models\textsuperscript{126,127}. One major drawback with this theory is that it fails at temperature far away from \( T_g \)\textsuperscript{88,128,129}. Also, at temperatures below \( T_c \), which is the characteristic temperature in IMCT predicting the divergence in dynamics, it fails to predict the power law divergence in the \( \alpha \)-relaxation time.

Failure of ideal mode coupling theory to predict \( \alpha \)-relaxation of glass-forming materials over a wide range of temperatures motivated Ken Schweitzer and co-workers to develop nonlinear Langevin equation (NLE) which predicts the hopping of a single particle in the mean field of other particles (Figure 2.6). Within this framework, barriers are finite below jamming and at nonzero temperature. The central concept of this theory is that at low temperatures when the liquids are sufficiently dense, the local cage scale hopping takes
place with increased participation from the surrounding medium. Initially, this framework was developed to understand the local uncooperative hopping in small molecule glass formers (particle fluids) and was later extended to predict the glass formation behavior in polymers by allowing the long range elastic distortion needed for cage-scale rearrangement. The overall activation barrier is the resultant of contributions from local cage hopping and the rearrangement of the overall medium to facilitate this hopping event. This facilitation of the overall rearrangement of the surrounding medium microscopically
couples the elasticity and the growing length scale of hopping. This intuitively means that glassy modulus plays an important role in determining the activation barriers in deeply super-cooled liquids.

2.4.3 Generalized localization model

We have seen and understood that the structural relaxation time ($\tau_\alpha$) of glass forming liquids shows a super-Arrhenius behavior with decrease in temperature (free volume models), and with this the particles solidify and localization occurs, which is characterized by a length scale. The elastic activated transport models, discussed in the previous section, assume that the relaxation occurs with particles escaping from the local potential wells (hopping). These approaches predict that the high-frequency shear modulus ($G_\infty$) of the material is central to predicting glass formation behavior. Dyre$^{99}$ and Nemilov$^{130}$ have argued that activation energy for transport increases proportional to $G_\infty$.

One measure of elastic modulus is local Debye-Waller factor $\langle u^2 \rangle$. This is defined as the average rattle amplitude of a particle trapped in a cage of particles on a picosecond time scale. The inverse of $\langle u^2 \rangle$, $k_m = kT/\langle u^2 \rangle$, is a measure of the local force constant. This value scales roughly with the high-frequency modulus$^{103, 108}$. $\langle u^2 \rangle$ is a high-frequency quantity and is easily accessible from simulations$^{3, 4, 131}$ and incoherent neutron scattering experiments$^{52}$. It has been shown by Hall and Wolynes$^{132}$ and Leporini et al.$^{101, 133}$ that this measure of shear modulus tracks significantly well with the predictions of elastically activated transport models of glass formation.
Now, it becomes very critical to understand the interrelations between the changes occurring in low-frequency dynamics (structural relaxation time) and high-frequency dynamics \( G \) or \( \langle u^2 \rangle \). In an attempt to understand these interrelations, Simmons et al.\(^3\) have combined Hall and Wolynes\(^{132}\) approach and free volume approach of Turnbull and Cohen\(^{134}\) to predict structural relaxation time and came up with a localization model for relaxation given by equation 2.21 using scaling relation of \( v_f \sim \langle u^2 \rangle^{\alpha/2} \) for free volume

\[
\tau = \tau_0 \exp \left[ \left( \frac{u_0^2}{\langle u^2 \rangle} \right)^{\alpha/2} \right] \tag{2.21}
\]

where \( \tau_0 \) is constant a prefactor, \( u_0^2 \) is the critical particle oscillation required to escape the cage, and \( \alpha \) depicts the anisotropy in the shape of free volume growth with temperature, with \( \alpha = 3 \) depicting a perfectly isotropic growth. All these quantities are fit parameters.

Betancourt et al.\(^{135}\) have further developed this model by reducing the number of fit parameters. They define \( \tau_0 \) and \( u_0^2 \) at the onset temperature, \( T_A \), making them measurable quantities rather than fit parameters. This reduces equation 2.21 to equation 2.22 leaving only one free parameter \( \alpha \).

\[
\tau \left( \langle u^2 \rangle \right) = \tau_A \exp \left[ \left( \frac{u_A^2}{\langle u^2 \rangle} \right)^{\alpha/2} - 1 \right] \tag{2.22}
\]

2.5 Overview of materials having dynamic interfaces

Polymers can be cast into very thin films of thickness ranging from a few microns to a few nanometers. This nanoscale confinement of glass-forming materials like polymers has a significant effect on these materials’ dynamic and mechanical properties, and hence
on their performance in nanoscale applications, such as electronics, solar cells, coatings, and membranes\textsuperscript{18,136,137}. For example, the glass transition temperature, $T_g$, of polymers under nanoconfinement can be dramatically increased or decreased compared to bulk values\textsuperscript{138,139}, and this alteration depends on system details. Being able to predict and control how glass formation and mechanical properties of polymers are altered under nanoconfinement is thus important for the optimal manufacture and use of such materials at the nanoscale. A large body of research over the past twenty years, ranging back to seminal studies by Keddie et al.\textsuperscript{19,140} and Jackson and McKenna\textsuperscript{141} has focused on understanding the dynamics and the glass transition in thin films.

2.6 Mobility at the interface of polymer thin films

In seminal work of Keddie, Jones and Cory on polystyrene thin films, they found that for films less than 40nm thick, $T_g$ of polystyrene film was reduced to a temperature way below than that of bulk $T_g$ of polystyrene. Figure 2.7 shows one such example from the work of Ellision et al.\textsuperscript{142} It was suggested that, at the interface of the polymer thin film, the material has different properties as compared to the bulk of the material. The interface of a freestanding polymer film has liquid-like behavior and this arises because of the lower activation energies for the chains present near the interface as compared to those in the bulk.

Recent work in this area focuses on developing experimental techniques to directly measure the dynamics at the free surface of thin films. These experiments indicate the existence of a relatively high mobile surface compared to the bulk of the material, and this mobile layer extends about 10nm into the bulk of the film. There are several orders of
difference in the mobility of these two regions and the surface layer tends to be mobile even below the glass transition of the bulk of the film. These results have been well supported from molecular dynamics simulations of polymer thin films, for both supported and unsupported films.

A lot of work has been done in investigating the thickness of this mobile layer. Probe reorientation technique has been used to study the dynamics of thin films over a wide range of temperature as shown in Figure 2.8. Here, we see that the thickness of the mobile layer of freestanding polystyrene films is about 7nm and decreases with decrease
in temperature. It is also observed that this length scale is independent of molecular weight of the sample, thickness of the sample and the kind of probe being used. A similar thickness of the mobile layer has been reported in supported polystyrene films\textsuperscript{33}.

Other experimental measurements on embedding gold nanoparticles into polystyrene surfaces have shown the existence of a highly mobile surface layer\textsuperscript{144–146}. Similar observations have been found in measuring the dynamics of freestanding and supported poly(methyl methacrylate) films. There are other experimental techniques like, dielectric measurements\textsuperscript{147,148}, measurements of dynamic heat capacity, and shear force modulation, that have not reported this enhancement in dynamics at the surface. In this context, it now becomes very important for us to understand the different techniques used to measure dynamics in thin films and the kind of measure they give.

Figure 2.8: Mobile surface layer thickness for polystyrene which depends upon temperature but does not depend upon total film thickness, polymer molecular weight, probe molecule identity, or temperature scanning rate. Reprinted with permission from reference\textsuperscript{143}. 

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2.7 Experimental techniques to measure dynamics in thin films

Due to the growing interest in understanding the behavior of material in very thin films, a lot of experimental techniques have been developed and employed to study the behavior of material under confinement. A few of them include ellipsometry, fluorescence molecular probe techniques, X-ray reflectivity, Brillouin light scattering, positronium lifetime spectroscopy, and dielectric measurements.

2.7.1 Ellipsometry

This technique is used for samples whose thickness ranges from a few microns to a few nanometers. This technique is based upon the changes that occur in the polarization of the light when passed through the thin film. The film thickness is determined by measuring the ellipsometric angles $\psi$ and $\Delta$ as a function of wavelength at a certain angle of incidence. Refractive index $n(\lambda)$ and then thickness of the film is determined by fitting the $\psi$ and $\Delta$ data as a function of wavelength to a Cauchy model.

2.7.2 Fluorescence techniques

These techniques measure the translational diffusion of a small molecule chromophore in thin films. Fluorescence nonradioactive energy transfer occurs when a polymer film containing chains doped with a donor chromophore is layered on top of a film comprising of acceptor chromophores. When the sample is annealed, the donor chromophores transfer their energy to acceptor chromophores when the latter diffuse across an interface and are in the distance of a few nanometers from the donor chromophore. This causes a decrease in fluorescence intensity and the net decrease can be quantified and associated with translational motion (diffusion) of acceptor chromophores.
2.7.3 X-ray reflectivity

When an X-ray beam is incident onto the flat surface of a thin film at a grazing angle smaller than the critical angle, total internal reflection takes place. X-ray reflectivity relates the variation of refractive index with change in wavelength. An X-ray reflectivity curve generally shows normalized intensity as a function of grazing angle. Interference between the reflected waves can be seen as oscillations on this curve. Thicker films lead to a shorter period of oscillations. The thickness of the films is obtained by Fourier transformation of this oscillatory curve and analyzing the peak position.

2.7.4 Brillouin light scattering (BLS)

BLS is a powerful technique to study the high-frequency elastic properties of thin films. BLS is carried out using a Fabry-Perot interferometer. Laser light of $\lambda = 514.5\text{nm}$ is focused and incident on to the sample at multiple angle of incidences. The backscattered light is collected using the same lens and is analyzed to determine the phonon velocity in the direction parallel to the surface of the thin film.

2.7.5 Dielectric spectroscopy (DS)

DS is one of the most commonly used techniques to measure dynamics of glass forming materials\(^6\)\(^,\)\(^7\). It gives us access to a very broad range of frequency spectrum over which we can study dynamics. This helps us better understand the slowing down of segmental relaxation as the material enters glass formation regime. To understand glassy dynamics, the most commonly measured quantity is the complex dielectric permittivity, $\varepsilon^* = \varepsilon' - i\varepsilon''$. The imaginary part, $\varepsilon''$ or dielectric loss, is plotted as a function of frequency to characterize the dynamics. Segmental relaxation leads to a peak in this plot and by
knowing the peak frequency, we can estimate segmental relaxation time to be \( \tau_\alpha = 1/(2\pi v_\alpha) \), where \( v_\alpha \) corresponds to peak frequency.

2.8 Discrepancy in measuring \( T_g \) from various experimental techniques

We see from above that different experimental techniques probe different material properties in order to predict the glass transition in thin films. Pseudo-thermodynamic measures of \( T_g \) from ellipsometry, calorimetry, etc. probe the changes in thermal expansion coefficient and are sensitive to the mean \( T_g \) of the film. These measurements are more biased toward regions of lower \( T_g \) and thus show greater suppression in \( T_g \) of thin films as compared to the bulk material. On the other hand, dynamic measure of \( T_g \) from dielectric spectroscopic measurements are an average of relaxation times across the film and consequently show lower supersession in \( T_g \) as compared to pseudo-thermodynamic measures. Ken Schweizer et al.\textsuperscript{154} have precisely shown this to be true from theoretical calculations of different measures of \( T_g \) and have concluded that the averaging scheme employed in different experimental measures is different and they report different averages of the same system. In this work, we attempt to deduce the weighting factors associated with pseudo-thermodynamic and dynamic measures of \( T_g \) and show that employing these weighting factors into the measures of \( T_g \) will result in a universal understanding of \( T_g \) suppression in polymer thin films.

2.9 Interfacial length scale associated with glass transition in thin films

All the prior studies on measuring dynamics in thin films confirm the existence of an interfacial dynamics gradient. But in some cases the nature and temperature dependence of this length scale vary from others. Paeng et al.\textsuperscript{143} have defined this length scale such
that they measure the fraction of the film that relaxes on a chosen time scale. They see an increase in this length scale upon increase in temperature (Figure 2.7). On the other hand, simulations of polymeric thin films have defined the interfacial scale to be the range over which dynamics return to bulk like behavior\textsuperscript{35–38,155}. This gives us a length scale that increases upon decrease in temperature. Lang et al.\textsuperscript{35} have shown that the interfacial dynamics length scale is primarily governed by the size of cooperatively rearranging regions (CRRs - from Adam-Gibbs\textsuperscript{156}) and these regions facilitate the propagation of surface dynamics into the bulk of the film. They show that the interfacial length scale measure by Paeng et al\textsuperscript{143} is qualitatively different from the interfacial length defined by them. The latter use a fixed temperature interfacial length while Paeng et al. use a fixed time scale interfacial length.

2.10 Effect of nanoconfinement on fragility of glass formation

In a fundamental sense, the fragility of glass formation is believed to reflect size of CRRs with more fragile materials having longer CRRs. Confining the material to the nanometer length scale will truncate the CRRs and this will be reflected in changes in fragility of thin films as compared to the bulk of the material. Many studies have shown that, indeed, we see a reduction in fragility of thin films relative to bulk\textsuperscript{157–160}. But this is not always the case and some studies have found that fragility is enhanced under nanoconfinement\textsuperscript{15,34,86}. Marvin et al.\textsuperscript{161} have shown that the mean fragility of the system is a segmental relaxation time weighted average of the local fragilities across the film. This means that mean fragility will be biased towards the slowest relaxing regions and this is the reason why systems showing an enhancement in dynamics at the interface tend to show
a suppression under nanoconfinement and systems showing suppression in dynamics at the interface tend to show an enhancement in the overall fragility under nanoconfinement.

2.11 Correlations between the bulk fragility and the $T_g$ - suppression under nanoconfinement

As the effect of nanoconfinement on the fragility is discussed in the previous section, it is of further interest to understand how the latter one influences the former one. For a long time, most of the studies in this field were dedicated to understanding the deviation in $T_g$ under confinement and less thought was given to addressing the question of why certain polymers show greater nanoconfinement effect compared to others under similar conditions. Evans et al.\textsuperscript{5} have shown by combining data from the literature and from their own experiments that there is a one-to-one correlation between the bulk fragility of the material and the suppression in $T_g$ under confinement. They found that PVC, which has the highest bulk fragility, showed highest suppression in $T_g$ while PS with 4% DOP, having the lowest bulk fragility, showed almost no suppression in $T_g$ under confinement.

In these studies, fragility was varied by altering composition, either by introducing an additive or by simply selecting a different polymer. As a consequence, it is difficult to draw firm conclusions regarding the generality and magnitude of the observed dependence of confinement effects on fragility, as factors such as chain chemistry, composition gradients, and so on may play a role, independent from fragility, in influencing the strength of nanoconfinement effects. Indeed, interfacial composition gradients were directly observed in Riggleman et al.’s study\textsuperscript{15}, raising the possibility that a difference in the chemical nature of the interface may have contributed to results.
In this chapter, we present in detail, the model used to simulate filled and unfilled bulk polymer systems and filled and unfilled free standing polymer thin films.

3.1 Standard bead spring model

Simulations employ an attractive bead-spring model polymer, extended from the earlier model of Kremer and Grest\textsuperscript{1,2}, that has been extensively employed to study polymer glass formation behavior\textsuperscript{1,3,4,30,65,162}. Within this model, non-bonded interactions are given by a 12-6 Lennard Jones potential:

\[
E_{ij} = 4\varepsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r} \right)^{12} - \left( \frac{\sigma_{ij}}{r} \right)^{6} \right]
\]

where \(\varepsilon_{ij}\) and \(\sigma_{ij}\) are Lennard Jones energy and range parameters, respectively, and where the interaction is truncated and shifted to 0 at \(r = 2.5\sigma\),\textsuperscript{163} except where otherwise noted. Bonded beads interact via the Finitely Extensible Nonlinear Elastic (FENE) potential:

\[
E_{\text{FENE}} = -0.5K_{\text{FENE}}R_0^2 \ln \left[ 1 - \left( \frac{r}{R_0} \right)^2 \right] + 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right] + \varepsilon
\]
where the first term sets a maximum bond length and the second term describes the Lennard-Jones repulsion. This bonding model has the advantage that it largely prevents aphysical chain-crossing events.

3.2 Bulk simulations of polymer/diluent blends

The host polymer consists of a melt of linear 20-bead chains, well below the entanglement limit of ~85 for this model\textsuperscript{164,165}. Non-bonded interactions between monomers employ standard values of $\epsilon_{pp}$ and $\sigma_{pp}$ equal to 1 and mass $m = 1$ (where subscript ‘$p$’ denotes the polymer repeat unit). Bonded interactions employ the standard FENE model with $K = 30$ and $R_0 = 1.5$. We also simulate a pure polymer melt comprised of chains that are 10 beads long, to compare and account for effect of chain length on glass formation behavior. We perform simulations of the 20-bead polymer in the pure state, in presence of a single bead diluents of size $\sigma$ equation to 1, 0.75, or 0.50, and in the presence of a series of oligomeric diluents of varying molecular stiffness ($K$).

Each oligomeric diluent molecule consists of a linear chain of 10 beads, where each bead is half the size of the polymer monomers ($\sigma_{oo} = 0.5$, and $\sigma_{po} = 0.75$, where subscript ‘$o$’ denotes the oligomer repeat unit) and where $\epsilon_{po} = 1.0$. In order to prevent oligomer aggregation in the limit of highly stiff chains, we employ $\epsilon_{oo} = 1.0$ but truncate the oligomer-oligomer LJ interaction at a range of $r = 2^{1/6}\sigma$, resulting in a purely repulsive interaction between oligomers. For the oligomeric additive only, we also introduce a cosine bending potential given by:

$$E = K\left[1 + \cos(\theta)\right]$$

3.3
where $\theta = \pi$ is the equilibrium bond angle and $K$ is the stiffness coefficient. In order to quantify the effect of oligomer stiffness on the polymer glass formation and mechanical behavior, we perform simulations with stiffness coefficient $K = 100, 50, 25, 10, 5, 3, 1.5, 0.5$ and $0$, with the $K = 0$ case modeled by omitting the bending potential entirely. Also, a 20 bead oligomeric diluent is simulated to account for the effect of varying additive length. Single bead diluents are modeled in a similar way as oligomeric diluents, except that the diluent – diluent LJ interaction is not set to purely repulsive interaction. We perform simulations with $\sigma_o = 0.5, 0.75$ and $1.0$ to capture the effect of additive bulkiness on the glass formation and mechanical behavior of the host polymer. In each case, the cross-sigma is given by the arithmetic mean of the polymer and diluent bead sigma’s.

Each simulation includes 80 polymer chains. Simulations with additives incorporate ~5% additive by volume, corresponding to 68 oligomer molecules or 674 single bead diluents with $\sigma = 0.5$ or 200 single bead diluents with $\sigma = 0.75$ or 85 single bead diluents with $\sigma = 1.0$. This concentration is chosen because previous work has indicated that antiplasticizer additives tend to exhibit a maximal effect at this concentration$^{1,79}$.

These set of simulations are carried out using the 22$^{nd}$ Feb, 2013 release of LAMMPS$^{166}$ (Large-scale Atomistic/ Molecular Massively Parallel Simulator) for all simulated systems except the case of oligomer diluent with $K = 0$, for which we used 28$^{th}$ May 2012 release of LAMMPS. All quantities are in dimensionless LJ units. Simulations employ the Nose-Hoover thermostat and barostat, as implemented in LAMMPS, with dampening coefficients for both thermostat and barostat equal to $2\tau_{LJ}^3$, where $\tau_{LJ}$ is the LJ unit of time. All simulations in the NPT ensemble are performed at pressure $P = 0$. 

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Because of the differences in particle mass and size in the various systems simulated, we employ slightly different timestep sizes in these systems to ensure good convergence with maximal simulation speed. Specifically, simulations of the pure polymer employ a rESPA (reversible reference system propagator algorithm) time integrator. 

Figure 3.1: Snapshot of a cross section of bulk simulation of (a) pure polymer (b) pure polymer/single bead additive blend (c) Pure polymer/oligomer additive blend with stiffness coefficient, K=5.0 (d) Pure polymer/oligomer blend with stiffness coefficient K=100.
allowing a different timestep to be used for integration of bonded and non-bonded interactions. A 4:1 ratio is employed between non-bonded and bonded timesteps, with an outer (non-bonded) timestep of $0.01\tau_{LJ}$. For the polymer/oligomer system, a time step of $0.002\tau_{LJ}$ is used for all interactions with a Verlet time integrator. For polymer/single bead diluent systems a rESPA integrator with a 4:1 ratio is employed between non-bonded and bonded timesteps, with an outer (non-bonded) timestep of $0.004\tau_{LJ}$ for $\sigma = 0.5$ and 0.75 and $0.01\tau_{LJ}$ for $\sigma = 1.0$.

In order to quantify glass formation behavior, we prepare simulated systems by quenching the material from high to low temperature and then performing a post-quench anneal at each temperature in order to obtain a well-defined temperature range of in-equilibrium configurations\textsuperscript{3,35}. Specifically, random configurations are initially generated in PACKMOL\textsuperscript{168} and equilibrated at $T = 1.5$ in the NPT ensemble for $10^4\tau_{LJ}$. The resulting configurations are then quenched in the NPT ensemble at a rate of $10^{-5} T/\tau_{LJ}$ to a minimum temperature of $T = 0.1$ while saving configurations at regular intervals. Configurations at each temperature are then subjected to an additional equilibration in the NPT ensemble for a duration specified in Table 3.1. Each simulation is then slightly rescaled to the average density at that temperature as determined from the second half of the equilibration runs and subject to an additional equilibration for a period of $10^3 \tau_{LJ}$ in the NVT ensemble prior to collection of data in the NVT ensemble. This annealing schedule is chosen to ensure an equilibration duration of at least $100\tau_\alpha$, where $\tau_\alpha$ is the segmental relaxation time at a specified temperature, up to a maximum computationally tractable equilibration time of $10^5\tau_{LJ}$. Throughout this paper, relaxation-time data is based purely on temperatures satisfying the above $100\tau_\alpha$ equilibration-length criterion. Mechanical and high-frequency
dynamic properties are reported at both in- and out-of-equilibrium temperatures, as in real glassy materials.

Once we capture the effect of backbone stiffness of oligomeric diluents (discussed in Chapter IV) on the glass formation behavior and mechanical properties of a pure flexible polymer, we carry out further set of simulations to understanding the effect of varying other molecular properties like, stiffness of polymer backbone (Table 3.2), and cross interaction parameter between the polymer and the diluent, $\epsilon_{ij}$ (Table 3.3). We also study the effect of varying additive concentration on the properties of pure flexible polymer (Table 3.4).

These set simulations are carried out using a similar quench, equilibration, and data collection protocol as described previously. They are carried out using the 7th Dec, 2015 release of LAMMPS. They employ a similar sample preparation protocol as described above but uses a slightly different equilibration scheme as shown in Table 3.5

Table 3.1: NPT equilibration time after quench for simulations of blends of flexible polymer and oligomer diluents of varying stiffness

<table>
<thead>
<tr>
<th>Temperature range</th>
<th>Equilibration length</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.0 \leq T \leq 1.5$</td>
<td>$10 000 \tau_{LJ}$</td>
</tr>
<tr>
<td>$0.7 \leq T &lt; 1.0$</td>
<td>$50 000 \tau_{LJ}$</td>
</tr>
<tr>
<td>$0.1 \leq T &lt; 0.7$</td>
<td>$100 000 \tau_{LJ}$</td>
</tr>
</tbody>
</table>
Table 3.2: Matrix of simulations carried out to predict structure property relationship in polymer diluent blends – effect of varying relative backbone stiffness of polymer and oligomer diluent at 5% by volume concentration of the diluent ($\epsilon_{ij} = 1.0$)

<table>
<thead>
<tr>
<th>$K_{\text{additive}}$</th>
<th>$K_{\text{polymer}}$</th>
<th>$K_p = 1.5$</th>
<th>$K_p = 3.0$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_a = 0.0$</td>
<td>$K_a = 0.0$</td>
<td>$K_a = 0.0$</td>
</tr>
<tr>
<td></td>
<td>$K_a = 0.5$</td>
<td>$K_a = 1.5$</td>
<td>$K_a = 1.5$</td>
</tr>
<tr>
<td></td>
<td>$K_a = 1.5$</td>
<td>$K_a = 3.0$</td>
<td>$K_a = 3.0$</td>
</tr>
<tr>
<td></td>
<td>$K_a = 10.0$</td>
<td>$K_a = 10.0$</td>
<td>$K_a = 10.0$</td>
</tr>
<tr>
<td></td>
<td>$K_a = 25.0$</td>
<td>$K_a = 25.0$</td>
<td>$K_a = 25.0$</td>
</tr>
<tr>
<td></td>
<td>$K_a = 100.0$</td>
<td>$K_a = 100.0$</td>
<td>$K_a = 100.0$</td>
</tr>
</tbody>
</table>

Table 3.3: Matrix of simulations carried out to predict structure property relationship in polymer diluent blends – effect of varying cross interaction parameter ($\epsilon_{ij}$) between polymer and oligomer diluents at 5% volume concentration of the diluent ($K_{\text{polymer}} = 0.0$)

<table>
<thead>
<tr>
<th>$K_a = 0.0$</th>
<th>$K_a = 25.0$</th>
<th>$K_a = 100.0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\epsilon_{ij} = 0.6$</td>
<td>$\epsilon_{ij} = 0.6$</td>
<td>$\epsilon_{ij} = 0.6$</td>
</tr>
<tr>
<td>$\epsilon_{ij} = 0.8$</td>
<td>$\epsilon_{ij} = 0.8$</td>
<td>$\epsilon_{ij} = 0.8$</td>
</tr>
<tr>
<td>$\epsilon_{ij} = 1.2$</td>
<td>$\epsilon_{ij} = 1.2$</td>
<td>$\epsilon_{ij} = 1.2$</td>
</tr>
<tr>
<td>$\epsilon_{ij} = 1.4$</td>
<td>$\epsilon_{ij} = 1.4$</td>
<td>$\epsilon_{ij} = 1.4$</td>
</tr>
</tbody>
</table>
Table 3.4: Matrix of simulations carried out to predict structure property relationship in polymer diluent blends – effect of varying the concentration of the oligomer diluent ($K_{\text{polymer}} = 0.0$). 1% and 3% indicate the volume concentration of diluent used.

<table>
<thead>
<tr>
<th>$K_a = 0.0$</th>
<th>$K_a = 25.0$</th>
<th>$K_a = 100.0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon_{ij} = 0.6 - 1%$ and $3%$</td>
<td>$\varepsilon_{ij} = 0.6 - 1%$ and $3%$</td>
<td>$\varepsilon_{ij} = 0.6 - 1%$ and $3%$</td>
</tr>
<tr>
<td>$\varepsilon_{ij} = 0.8 - 1%$ and $3%$</td>
<td>$\varepsilon_{ij} = 0.8 - 1%$ and $3%$</td>
<td>$\varepsilon_{ij} = 0.8 - 1%$ and $3%$</td>
</tr>
<tr>
<td>$\varepsilon_{ij} = 1.2 - 1%$ and $3%$</td>
<td>$\varepsilon_{ij} = 1.2 - 1%$ and $3%$</td>
<td>$\varepsilon_{ij} = 1.2 - 1%$ and $3%$</td>
</tr>
<tr>
<td>$\varepsilon_{ij} = 1.4 - 1%$ and $3%$</td>
<td>$\varepsilon_{ij} = 1.4 - 1%$ and $3%$</td>
<td>$\varepsilon_{ij} = 1.4 - 1%$ and $3%$</td>
</tr>
</tbody>
</table>

Table 3.5: NPT equilibration time for simulations listed in Table 3.2 Table 3.3, and Table 3.4

<table>
<thead>
<tr>
<th>Temperature range</th>
<th>Equilibration length</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.0 \leq T \leq 1.5$</td>
<td>$10 000 \tau_{LJ}$</td>
</tr>
<tr>
<td>$0.7 \leq T &lt; 1.0$</td>
<td>$50 000 \tau_{LJ}$</td>
</tr>
<tr>
<td>$0.1 \leq T &lt; 0.7$</td>
<td>$100 000 \tau_{LJ}$</td>
</tr>
</tbody>
</table>

3.3 Bulk simulations of polymer of varying bond length

In a prior work, Mackura et al.\textsuperscript{169} have shown that by systematically altering the FENE parameters, shown in Table 3.6, alters bond length and preserves to leading order, the fluctuation behavior of the bonds and can therefore be expected to preserve the chain uncrossability characteristic of the standard Kremer-Grest model. We employ a similar
sample preparation protocol as described in previous sections. The equilibration protocol for this set of simulations is shown in Table 3.7.

3.4 Freestanding thin film simulations of polymer/diluent blends and polymers of varying bond length

We perform molecular dynamics simulations of freestanding films comprised of unentangled 20-bead linear bead-spring polymer chains with and without the addition of diluents. A series of neat polymer films is simulated in which the backbone bond length is varied (equilibrium bond lengths are set to 0.96, 0.88, 0.83, and 0.79 in four different models). We also simulate a series of films comprised of polymer/diluent blends, in which the polymeric component is identical to the chain with bond length 0.96 in the bond-length study. Diluents consist of 5% by volume of a monomeric diluent or one of several oligomer diluents of varying backbone stiffness. These additives are selected based on the results we describe in Chapter IV, to yield a range of modifications in the \( T_g \) and fragility of the bulk polymer system. Finally, the stiffness of two of the oligomeric additives is enhanced beyond the standard freely jointed chain by imposing an angular potential of the form described by equation 3.3. The angular stiffness parameter \( K \) is set to 5 for moderate stiffness and to 100 for high stiffness, similar to the bulk simulation described in the previous section.

For each of the simulated systems, four independent trials are performed. Initial random configurations are generated with the polymer chains in a freestanding film morphology using PACKMOL\textsuperscript{170}. The freestanding film morphology is then maintained by employing periodic boundary conditions in all directions and performing simulations in the NVT ensemble with a substantial gap above and below the film. Despite these
simulations nominally being performed in the constant volume ensemble, the presence of a free surface dictates that the polymer effectively follows constant pressure behavior with normal pressure $P = 0$. Configurations are initially equilibrated at a temperature of $T = 1.5$ for a time of 10,000 $\tau_{LJ}$. The systems are then quenched from 1.5 $T$ to 0.3 $T$ at a rate of $10^{-5} T/\tau_{LJ}$. Configurations saved regularly during the quench are then subject to an additional equilibration of at least 100 $\tau_\alpha$, where $\tau_\alpha$ is the structural relaxation time as determined from the self-part of the intermediate scattering function. Data collection runs are then performed from these resulting configurations for a time roughly equal to time of equilibration.

Table 3.6: FENE parameters for changing bond length

<table>
<thead>
<tr>
<th>FENE Parameters</th>
<th>Bond Length</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_0 = 1.5; \sigma = 1.0$</td>
<td>0.96</td>
</tr>
<tr>
<td>$R_0 = 1.4; \sigma = 0.9$</td>
<td>0.88</td>
</tr>
<tr>
<td>$R_0 = 1.35; \sigma = 0.85$</td>
<td>0.83</td>
</tr>
<tr>
<td>$R_0 = 1.3; \sigma = 0.8$</td>
<td>0.79</td>
</tr>
</tbody>
</table>

Table 3.7: NVT equilibration time for freestanding thin film simulations

<table>
<thead>
<tr>
<th>Temperature Regime</th>
<th>Equilibration length</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.0 \leq T \leq 1.5$</td>
<td>10 000 $\tau_{LJ}$</td>
</tr>
<tr>
<td>$0.7 \leq T &lt; 1.0$</td>
<td>50 000 $\tau_{LJ}$</td>
</tr>
<tr>
<td>$0.1 \leq T &lt; 0.7$</td>
<td>100 000 $\tau_{LJ}$</td>
</tr>
</tbody>
</table>
These thin film simulations are compared to simulations of the same set of polymers and polymer/additive blends in the bulk. In the thin film simulations, the polymeric materials is allowed to fill the entire box, with periodic boundary conditions in all directions and the box size subject to barostatting at 0 pressure via the Nose-Hoover barostat as implemented in LAMMPS. Other than this change of nominal ensemble, simulations are performed the same way through the end of isothermal equilibration. After this step, each simulation is resized to the mean density at that temperature as determined via an average over the second half of the equilibration runs for all four independent trials. Systems are then subject to a brief equilibration in the NVT ensemble, after which data is collected in the NVT ensemble.

Simulations are performed in the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) package. Simulations employ several time integration schemes determined based on computational efficiency and energy conservation tests in an initial round of pilot simulations. Specifically, simulations of pure polymer systems employ a RESPA time integrator with a timestep of 0.01 \( \tau_{LJ} \) for nonbonded interactions and a timestep of 0.0025 \( \tau_{LJ} \) for bonded interactions. In polymer/monomer blends, the smaller bead size necessitates shorter time steps - 0.004 \( \tau_{LJ} \) for nonbonded interactions and 0.001 \( \tau_{LJ} \) for bonded interactions. Simulations of polymer/oligomer blends employ a Verlet integrator with a timestep of 0.002 \( \tau_{LJ} \). Temperature is controlled via the Nose-Hoover thermostat, as implemented in LAMMPS, with a damping parameter of 2 \( \tau_{LJ} \). The net linear momentum is set to zero every 1 \( \tau_{LJ} \) through equilibration to prevent any possible buildup of momentum.
3.5 Analysis methods

The analysis methods used for looking at the simulation data are described in detail in the following section.

3.5.1 Analysis of low-frequency dynamics

Structural relaxation dynamics are quantified based on the self-part of intermediate scattering function\textsuperscript{173} given by:

$$F_s(k,t) = \frac{1}{N} \sum_j \langle \exp \left[ -ik \cdot (r_j(t) - r_j(0)) \right] \rangle$$

where $k$ is the wavevector, $N$ is the number of particles, and $r_j(t)$ is the position of particle $j$ at time $t$. We average over wavevectors with wavenumber $k = 7.07$, comparable to the first peak in the monomer structure factor data. Throughout this study, $F_s(k,t)$ is computed for the polymer segments only, to focus on alterations in polymer dynamics. Consistent with other recent work\textsuperscript{174,175}, the structural relaxation time $\tau_\alpha$ is defined as the time at which $F_s(k,t)$ decays to 0.2, employing a fit to a Kohlraush-Williams-Watt (KWW) stretched exponential,\textsuperscript{176,177}

$$F_s(k,t) = A \exp \left[ \left( \frac{t}{\tau_{KWW}} \right)^{\beta_{KWW}} \right]$$

to $F_s(k,t)$ at times after the inertial fast relaxation process ($\sim 1$ $\tau_{LJ}$) is complete, for data smoothing and interpolation.

In order to account for the time-scale limitations of molecular simulations in determining $T_g$, we quantify $T_g$ via four different protocols, consistent with other recent
simulation work\textsuperscript{161}. First, data for each system for $\tau_\alpha$ vs. $T$ are fit to the Vogel-Fulcher-Tammann\textsuperscript{114-116} equation.

$$\tau = \tau_0 \exp \left( \frac{D T_0}{T - T_0} \right)$$

A computational dynamic $T_g$, denoted $T_g^C$, is then defined as the temperature at which the system begins to fall out of equilibrium on a simulation time scale ($\tau_\alpha = 10^3 \tau_{LJ}$), using the VFT fit to in-equilibrium temperatures only for data smoothing. Similarly, an extrapolated experimental dynamic $T_g$, denoted $T_g^E$, is defined as the temperature at which this VFT fit extrapolates to a timescale associated with the experimental $T_g$ ($\tau_\alpha = 10^{14} \tau_{LJ}$, approximately equivalent to 100s). Third and fourth, pseudo-calorimetric and pseudo-volumetric $T_g$’s are defined based on the location of a change in slope of the temperature dependence of the system’s energy and volume respectively. This is done based on a fit of each of these quantities to the form\textsuperscript{178}.

$$h(T) = w \left( \frac{M_l - G_v}{2} \right) \ln \left[ \cosh \left( \frac{T - T_g}{w} \right) \right] + \left( T - T_g \right) \left( \frac{M_l + G_v}{2} \right) + c$$

where, $h(T)$ is any quantity which varies linearly over some temperature range below and above $T_g$. $M_l$ and $G_v$ are the slopes of the curve in the melt and glass, respectively, $w$ is a measure of the width over which the pseudo-thermodynamic glass transition occurs, and $c$ is the value of $h$ at $T_g$. These $T_g$’s are denoted by $T_g^{Cp}$ (pseudocalorimetric) and $T_g^v$ (volumetric). Computational and extrapolated values of $m$ are obtained by evaluating the following definition at $T_g^C$ and $T_g^E$ respectively:
\[
m = \left. \frac{\partial \log \tau_\alpha}{\partial \left( T_g / T \right)} \right|_{T = T_g}
\]

As discussed in the results section, an important characteristic temperature in application of the Generalized Localization Model is the onset temperature of glass formation \( T_A \). \( T_A \) is generally defined as the temperature below which \( \tau_\alpha \) first deviates from an Arrhenius temperature dependence\(^{179} \). Consistent with this definition, we compute \( T_A \) by determining the temperature at \( \tau_\alpha \) first deviates by 10\% from an Arrhenius fit to high-temperature relaxation data\(^{35} \).

### 3.5.2 High frequency dynamics

The Debye-Waller Factor, \(<u^2>\) is defined as the segmental mean-square displacement at a time near \( \tau_{LJ} \), consistent with other recent work\(^3,101,180 \). Specifically, it is determined at times of 0.985\( \tau_{LJ} \) for the pure polymer, 0.984\( \tau_{LJ} \) for polymer/oligomer blends, and 0.949\( \tau_{LJ} \) for the polymer/single-bead additive blends. These times correspond to the closest times saved to 1 \( \tau_{LJ} \) for each of the simulated systems.

### 3.6 Identification of the thermodynamic interface and binned analysis of free standing thin films

In order to quantify dynamics locally within film simulations, we sort particles into spatial bins of thickness 0.875\( \sigma \) as a function of distance from the interface, with the interface defined as the point at which the density is equal to half that in the film center. For the purpose of determining interfacial position, the density is calculated for bins with thickness of less than 0.16\( \sigma \). We first identify the film center by identifying the point halfway between the two positions at which the density is equal to 0.5; the central film
density is then determined based upon the average over a region at least 1 \( \sigma \) thick centered on this point. A precise position for the interface is determined by performing a linear interpolation using the two consecutive bins with values on either side of half of the central density. We denote the position of the interface as \( z = 0 \) and average all \( z \)-dependent data over the two interfaces. Once particles are sorted into bins based on their spatial position at each time, the relaxation time can then be computed on a per-bin basis via the protocol described in section 3.5.1.

Figure 3.2: Schematic representation of binning in a free standing thin film. Position of mid film (central red line) and bin interfaces (top and below red lines) are not drawn to scale. Numbers beside bins represent the mid-point position of that bin. The \( z \)-axis (direction of film thickness) is shown. Positive and negative \( z \)-directions represent the direction of the distance from the interface.
CHAPTER IV
TUNING POLYMER GLASS FORMATION BEHAVIOUR AND MECHANICAL PROPERTIES WITH OLIGOMERIC DILUENTS

4.1 Introduction

Introduction of a molecular diluent – a low-volume-fraction additive – is one of the longest-standing methods of modifying a polymer’s properties without dramatically altering its chemistry. Diluents can improve a polymer’s performance, inducing changes in its glass transition temperature \( T_g \), structural relaxation time \( \tau_\alpha \), moduli, and other related properties. Although diluents have traditionally been divided into two classes – plasticizers and antiplasticizers – recent evidence indicates that their array of possible effects is far richer than suggested by this binary classification scheme\(^2,7\). For example, observed diluent effects include suppression of \( T_g \) and the high-frequency glassy modulus \( G_\infty \) (plasticizers), suppression of \( T_g \) coupled with low-temperature enhancement of \( G_\infty \)\(^{1,6,10,11,65} \) (antiplasticizers), suppression of \( T_g \) with high-temperature enhancement of \( G_\infty \)\(^7\), and enhancement of \( T_g \)\(^{12}\). These examples illustrate that diluents can independently tune low-frequency dynamics (as reflected in \( T_g \)) and high-frequency dynamics (as reflected in \( G_\infty \)) in a temperature-dependent manner\(^{1–3,6,15,181}\), suggesting new opportunities for diluent-based rational polymer design. Leveraging these opportunities will require a deeper understanding of diluent effects, accounting for potentially distinct, temperature
dependent impacts on high- and low-frequency dynamics.

Here we employ molecular dynamics simulations of polymer/diluent blends to guide selection of diluent molecular properties producing targeted alterations in polymer linear-regime dynamics. Inspired by recent predictions of the Generalized Entropy Theory (GET) of glass formation\textsuperscript{2,103}, which is based on an extension of the Adam-Gibbs theory of glass formation\textsuperscript{156}, we focus on the role of diluent molecular stiffness in determining these alterations. Simulation details are discussed in detail in Chapter 3. In summary, we simulate a melt of attractive, unentangled bead-spring polymer chains\textsuperscript{182}, in which non-bonded beads interact via a 12-6 Lennard-Jones potential with characteristic energy $\varepsilon$ and length scale $\sigma$, with both values equal to one for the polymer. In addition to a pure ‘reference’ melt, we introduce 5\% by volume of diluents ranging from single beads to stiff oligomers, with this volume fraction chosen because it corresponds to a concentration at which antiplasticizers often exhibit a maximum effect\textsuperscript{79}. Consistent with prior work on polymer/diluent blends, we focus on the case where $\sigma$ for diluent beads is half of that for polymer beads, mimicking commonly ‘bulkier’ chemical moieties in polymer chains as compared to small-molecule diluents\textsuperscript{1,3,4,65}. Glass formation is simulated via a quench-and-anneal procedure that is inspired by experimental glass formation and is widely used in the literature\textsuperscript{1,3,15,35,42,183}.

4.2 Results and discussion

This section presents detailed discussion of the effects of varying molecular properties of diluents on the polymer glass formation behavior and mechanical properties.
4.1.1 Effect of varying backbone stiffness of oligomer diluent

We begin by characterizing diluent-induced alterations in the polymer’s low-frequency dynamics as quantified by $\tau_\alpha$, defined here as the time at which the self-part of the intermediate scattering function, calculated for the polymer segments only, decays to a value of 0.2. This yields results comparable to time-resolved incoherent neutron scattering. From this data, we determine $T_g$ via two conventions to account for the gap between computationally-accessible times and the time scale of the laboratory $T_g$: we obtain a ‘computational’ dynamic $T_g$ based on the temperature $T_g^c$ at which simulations fall out of equilibrium on a timescale of $10^3 \tau_{LJ}$ (the LJ unit of time) and an ‘extrapolated’ $T_g$ at the temperature $T_g^e$ at which a Vogel-Fulcher-Tammann$^{114-116}$ fit to in-equilibrium $\tau_\alpha$ data extrapolates to $10^{14} \tau_{LJ}$, corresponding to a ~100s experimental $T_g$ convention. We additionally compute computational-timescale $T_g$’s via two pseudothermodynamic conventions: a calorimetric temperature $T_g^{Cp}$ at which the energy vs temperature curve changes slope, and an analagous dilatometric temperature $T_g^v$. However, recent work has emphasized the insufficiency of $T_g$ as a measure of low-frequency structural relaxation$^{30,161,181}$, because changes in the temperature-breath of the glass transition can decouple shifts in $\tau_\alpha$ from shifts in $T_g$.$^{1-3,6,15,181}$ These changes are commonly quantified via the kinetic fragility index, $m$. As with $T_g$, we compute computational and extrapolated values of $m$ ($m^c$ and $m^e$, respectively) by applying its definition at $T_g^c$ and $T_g^e$, respectively. As shown in Figure 4.1, results are qualitatively insensitive to the choice of $T_g$ and $m$ convention. Except where noted, throughout this paper, standard deviations on plotted data, as determined from four independent runs, are similar to or fall within the size of the points.
To isolate the effects of diluent chemical bulkiness, degree of polymerization, and...
stiffness, we perform a series of simulations building up to stiff oligomers in a stepwise fashion. First, we introduce a diluent consisting of individual beads of size $\sigma = 1$, equal to the chain monomers. As shown by Figure 4.1 (a) and (b), this diluent has little effect on

Figure 4.1: (c) Scaled $T_g$ and $m$ as calculated via conventions described in the text as a function of oligomer stiffness; (d) Test of equation 2.1 for all systems in this study, with symbols having the same meaning as in part (b). Average uncertainty on x-axis of part (d) is 0.03.
polymer segmental dynamics at this volume fraction $\phi$. Maintaining the same $\phi$, we then reduce diluent size to $\sigma = 0.75$ and 0.5, which reduces $T_g$ and $m$, consistent with results in prior simulations$^{1,3,15}$. Given the weak alterations induced by the $\sigma = 1.0$ diluent (or upon reducing chain length from 20 to 10 in a pure melt, shown in Figure 4.1(b), this suppression must emerge from alterations in molecular packing upon mixing moieties of different chemical bulkiness rather than from chain-end-concentration effects. Indeed, the GET predicts a reduction in $T_g$ and $m$ upon introduction of small-molecule diluents, driven by shifts in configurational entropy associated with alterations in molecular packing efficiency$^2$. It also suggests that reductions in free volume generally correlate with suppression of fragility$^{109}$; suppression of $m$ with reducing bulkiness of a single-bead diluent can then be understood as emerging from densification upon mixing different size

Figure 4.2: Incipient crossover to suppression of $\tau_\alpha$ at low temperatures in the presence of the 10-bead additive
moieties. This connection to free volume theory is understood within the GET as emerging from a rough correlation between free volume and configurational entropy\(^{103,179}\).

Next, to study the role of oligomeric diluents, we simulate systems in which the diluent beads are polymerized to form oligomers with several degrees of polymerization \(n\). To prevent stiffness-driven aggregation, we render the oligomer-oligomer interaction purely repulsive by truncating the nonbonded potential at its minimum. Relative to the \(\sigma = 0.5\) diluent, diluent polymerization substantially increases \(T_g\) while modestly enhancing \(m\). These shifts reflect a net enhancement in \(\tau_\alpha\) at high temperature but an incipient crossover to suppression of \(\tau_\alpha\) at low temperatures in the presence of the 10-bead additive, apparent from VFT extrapolations of the data (Figure 4.2).

Finally, to probe the effect of diluent stiffness, we begin with this flexible oligomer with \(n = 10\) and subject it to a cosine bending potential \(E_{\text{bend}} = K[1 + \cos(\theta)]\), with spring constant \(K\) ranging, in LJ units, from 0 (flexible) to 100 (nearly rod-like). As shown in Figure 4.1(a-c), introducing diluent stiffness enhances polymer \(\tau_\alpha\), leading to a disappearance of the crossover in \(\tau_\alpha\) and an increase in both \(T_g\) and \(m\). A crossover to enhancement of \(T_g\) is observed prior to a crossover to enhancement of \(m\), such that by selecting an appropriate stiffness it is possible to suppress both relative to the pure polymer, increase \(T_g\) but decrease \(m\), or increase both. \(T_g\) and \(m\) for polymer/oligomer blends exhibit a rough linear correlation (Figure 4.1(c)) that is observed in a wide range of weakly interacting polymeric systems\(^{184}\). However, this does not include the pure polymer system or the single bead systems with \(\sigma \neq 0.5\). Again, this can be rationalized based upon the GET, which predicts that reductions in free volume generally
correlate with a fragility reduction, but can correlate with either suppressed or enhanced $T_g$. Alterations in molecular packing efficiency can therefore decouple $T_g$ and $m$.

As shown by Figure 4.1(c), the effects of diluent stiffness on $T_g$ and $m$ saturate for high $K$, with a dependence that does not obey any simple functional form. To understand the nature of this dependence, we draw inspiration from a recent study of the effect of a confining interface on a polymer’s glass transition. That study identified a relationship between nanoconfinement-induced $T_g$-shifts and the stiffness of the confining material as measured by its Debye-Waller factor $\langle u^2 \rangle$, which is a measure of segmental rattling volume on a ps timescale and exhibits an inverse proportionality with the high frequency modulus, $G_\infty \propto kT/\sigma \langle u^2 \rangle$. Specifically, it found that

$$\frac{T_g}{T_g^{\text{bulk}}} = \frac{T_g^{\text{fs}}}{T_g^{\text{bulk}}} + B \exp \left(-C \frac{\langle u^2 \rangle_{\text{confining}}}{\langle u^2 \rangle_{\text{bulk}}} \right)_{\text{fit}}$$

where $\langle u^2 \rangle$ is defined as mean square displacement at $1 \tau_{\text{LJ}}$ (roughly 1 ps), $T_g^{\text{fs}}$ is the $T_g$ of the polymer in contact with a completely soft interface (ie. $\langle u^2 \rangle \rightarrow \infty$), such as a free surface, $B$ and $C$ are fitting parameters, and subscripts “confining” and “bulk” denote values for the confining material and bulk polymer, respectively.

Equation 4.1 is consistent with the intuition that contact with harder confining surfaces, as defined by the high-frequency modulus, should more severely restrict relaxation. It is reasonable that an analogous form could describe blends of polymers with diluents of varying stiffness: a stiff diluent molecule, as defined by a low relative $\langle u^2 \rangle$ or high $G_\infty$, imposes an internal constraint impeding segmental relaxation. There is also a phenomenological basis for seeking parallels between these systems: prior studies have
noted parallels between glass formation under nanoconfinement and in nanocomposites\textsuperscript{188,189}; nanocomposites, in turn, share phenomenology with polymer/diluent blends. Consistent with this view, several prior studies have indicated the presence of strong interactions between nanoconfinement effects and diluent effects on the glass transition\textsuperscript{14,15,79,106}, suggesting possible overlap in their mechanistic origins. We therefore test whether a form equivalent to equation 4.1 also describes the variation of blend $T_g$ with diluent stiffness, making several modifications for applicability to this new system. First, in the context of diluent/polymer blends, the logical equivalent of $T_g^{\beta}$ is a term quantifying the extrapolation $T_g^{\text{soft}}$ of $T_g$ in the limit of an infinitely soft diluent (ie. a hypothetical diluent with $G_\infty = 0$ or $\langle u^2\rangle \to \infty$). For a thin film, this is realized in a freestanding film geometry; in polymer/diluent blends it is an extrapolation. Second, because these simulations consider beads of distinct sizes, we include the factor $\sigma$ in the inverse proportionality between $G_\infty$ and $\langle u^2\rangle$, leading to the equation

$$
\frac{T_g}{T_g,\text{pure}} = \frac{T_g^{\text{soft}}}{T_g,\text{pure}} + B \exp\left(-C \frac{\sigma_d \langle u^2 \rangle_d}{\sigma_{\text{pure}} \langle u^2 \rangle_{\text{pure}}} \right)_{T_g,\text{pure}}
$$

4.2

where subscripts $\text{pure}$ and $d$ denote properties for the pure polymer and diluent, respectively. As shown by Figure 4.1(c), this form describes $T_g$ data for all systems included in this study (R$^2$ is 0.98 for $T_g^c$ or 0.92 for $T_g^E$). This remarkably general result implicates $\langle u^2 \rangle$ and $G_\infty$ as fundamental properties determining glass-formation behavior, conceptually consistent with the elastically cooperative activated barrier hopping theory\textsuperscript{190,191}, which predicts that the glassy modulus plays a key role in determining activation barriers in supercooled liquids. While this study does not examine the role of
Figure 4.3: (a) Apparent Young’s modulus and (b) $kT/\langle u^2 \rangle$ for polymer beads vs temperature; (c) diluent-induced shift in apparent high frequency activation enthalpy vs entropy determined from equation 4.4, with symbols denoting the same systems as Figure 4.1(b); inset shows $\Delta H_a$ (red circles) and $\Delta S_a$ (blue squares) vs oligomer stiffness. In part (a), error bars shown for pure polymer are qualitatively characteristic of uncertainties in all systems shown.
polymer/diluent interaction strength, the original development of equation 4.2 suggests that its parameter $B$ is proportional to the strength of these interactions.

The above analysis indicates that the high-frequency dynamics of a diluent mediate its impact on polymer glass formation. We continue by assessing the impact of diluent stiffness on the high-frequency dynamics and mechanics of the polymer itself. These effects are most commonly quantified by alterations in the glassy modulus. As shown by Figure 4.3(a), the glassy Young’s Modulus of these systems as measured within the linear regime of a uniaxial deformation simulation at a rate of $10^4 \sigma/t_{LJ}$ (where $\sigma$ is the LJ unit of distance), is enhanced upon addition of all oligomeric additives. As shown by Figure 4.3(b), $kT/<u^2>$, which, as described above, is proportional to $G_c$, exhibits qualitatively equivalent trends. Notably, the oligomer stiffness yielding the greatest modulus-enhancement is observed to change upon cooling the system through a temperature modestly below $T_g$: at high temperature, a stiff oligomer yields the most stiffening; at low temperature, the most flexible oligomer yields the most stiffening.

This observation seems counterintuitive: one might expect a molecularly stiff diluent to yield, at all temperatures, a higher modulus than a flexible additive. To understand this observation, we make use of a body of theory\textsuperscript{99} treating $<u^2>$ as an effective free-energy activation barrier for local relaxation. The simplest such theory is that of Hall and Wolynes\textsuperscript{132}, which suggests that

$$\frac{G_n}{kT} \propto \frac{\mu_0^2}{<u^2>}$$

4.3
interpreted as a critical distance a segment must travel to escape its local minimum. This

\[ \frac{kT}{\langle u^2 \rangle} = \frac{H_a}{u_0^2} - \frac{S_a}{u_0^2} T \equiv \hat{H}_a - \hat{S}_a T \quad \text{(4.4)} \]

where \( H_a \) and \( S_a \) are the activation enthalpy and entropy of local relaxation.

The slope and intercept of the glassy modulus in Figure 4.3(a) or \( kT/\langle u^2 \rangle \) in Figure 4.3(b) can be interpreted as relating to an entropy and enthalpy, respectively, for local relaxation, similar to an approach for quantification of diluent effects on the dielectric beta relaxation time.\(^7\) As shown in Figure 4.3(c), \( \hat{H}_a \) and \( \hat{S}_a \), as computed from \( kT/\langle u^2 \rangle \), track together as oligomer stiffness is varied. This effect, known as entropy-enthalpy compensation\(^6,7\), explains the above trend in glassy modulus as a function of diluent stiffness: lower stiffness yields a higher favorable \( \Delta S_a \) for high-frequency relaxation than a stiff additive, consistent with weaker constraints imposed by its more flexible backbone; these weaker constraints allow better molecular packing (Figure 4.4), which yields a higher \( \Delta H_a \). The outcome of this tradeoff is a higher modulus at low temperature but a lower modulus at high temperature. At an intermediate “compensation temperature” of \( \sim 0.54 \), given by the slope of the line in Figure 4.3(c), the modulus of these systems nearly intersects. Identification of this temperature is essential to design of polymer/diluent blends, since in its vicinity modulus may be insensitive to diluent molecular stiffness. The pure polymer and blends involving single-bead diluents do not fall into this trend, likely for the same packing-related reasons that these systems do not exhibit the same proportionality of \( T_g \) and \( m \) as the oligomeric additives.
Consistent with the literature, the above results indicate that diluents’ effects on low- and high-frequency dynamics do not always track with one another; enhancement of modulus can accompany either enhancement or suppression of $\tau_\alpha$ and $T_g$. How are we to understand the relationship between these effects?

To answer this question, we turn again to the body of literature\textsuperscript{99}, of which the Hall-Wolynes theory is a seminal example\textsuperscript{132}, attempting to understand glass formation in terms of relationships between $\tau_\alpha$ and high-frequency dynamic properties such as $G_\infty$ and $\langle u^2 \rangle$. We focus on the “Generalized Localization Model” (GLM) for supercooled liquid

Figure 4.4: Scaled occupied volume fraction vs temperature. Label in this figure is same as in Figure 4.1(b)
Figure 4.5: (a) $\ln \tau_A$ vs $1/\langle u^2 \rangle$ for chain monomers; (b) GLM collapse of this data via equation 4.5; (b inset) $\alpha$ from the GLM vs oligomer stiffness, with error bars corresponding to 95% confidence intervals on fit values.
relaxation\textsuperscript{4,135}, which has been found to describe a number of systems\textsuperscript{4,100,192,193} based on the following relationship between $\tau_\alpha$ and $\langle u^2 \rangle$:

$$\tau_\alpha = \tau_A \exp \left( \left( \frac{u_A^2}{\langle u^2 \rangle} \right)^{\alpha/2} - 1 \right)$$

4.5

where $\alpha$ is interpreted, based on the free volume model underlying this equation, as being a measure of the anisotropy of local caging volume, with $\alpha=3$ denoting isotropic free volume and $\alpha>3$ denoting anisotropic free volume, and where $\tau_A$ and $\langle u_A^2 \rangle$ are the values of $\tau_\alpha$ and $\langle u^2 \rangle$ at the onset temperature $T_A$ of glass formation. As shown by Figure 4.5, equation 4.5 leads to a collapse of $\tau_\alpha$ vs $\langle u^2 \rangle$ data for all systems in this study despite use of only one adjustable parameter. Within the GLM, shifts in $\alpha$ observed with varying diluent stiffness (see Figure 4.5(b), inset) suggest that these diluents decouple high- and low-frequency dynamics by altering the local anisotropy of free volume. However, the observation of $\alpha$ generally less than 3 is inconsistent with the scaling model underlying this interpretation. Instead, this functional form can be rationalized based on an elastic localization framework such as the Hall-Wolynes theory, in which case values of $\alpha$ greater than 2 can be interpreted as indicating anharmonic particle caging. The exact relationship of the variation in $\alpha$ with oligomer stiffness or other molecular properties remains an open question that should be a focus of future research.

Following this, it would be intuitive for us to understand the effect of varying other variables like the stiffness of polymer host polymer, and the cross interaction between the polymer and oligomer diluents. It would be interesting to see if equation 4.2 still holds up in these systems and is it universal?. If not, it would be fruitful to further investigate into
developing a universal relation to predicting the interrelations between high-frequency and low-frequency dynamics with polymer/diluent blends.

4.2.2 Effect of varying backbone stiffness of polymer

Figure 4.6: $\tau_\alpha$ vs. temperature for neat polymer of varying backbone stiffness

Figure 4.7: $kT/\langle u^2 \rangle$ vs. temperature for neat polymer of varying backbone stiffness
Figure 4.8: (top) $\tau_\alpha$ vs temperature for systems shown in the legend ($K_{\text{Polymer}} = 1.5$) (bottom) $\tau_\alpha$ vs temperature for systems shown in the legend ($K_{\text{Polymer}} = 3.0$). ‘Pure’ in the legend refers to unfilled polymer matrix.
These set of simulations are very much identical to the one’s described in the previous section, except for, the polymer matrix in these simulations has a certain degree of backbone stiffness associated with it. Here, we characterize the diluent induced alterations in a similar manner as described in the previous section. Figure 4.6 shows the plot for $\tau_\alpha$ determined from the decay of self-part of intermediate scattering function for neat polymer of varying backbone stiffness. Stiffness of polymer backbone is modified in a similar fashion employed for modifying diluents’ stiffness. Figure 4.6 shows that an increment in the backbone stiffness of the polymer tends to slower the relaxation behavior of polymer chains causing an increase in glass transition temperature and breadth of glass transition s characterized by fragility, $m$.

Figure 4.7 shows the changes in the local modulus of the material as quantifies by $kT/\langle u^2 \rangle$. We observe a suppression in the local modules of the material with increase in the backbone stiffness of polymer chains. This is consistent with experimental observations.

![Figure 4.9: Diluent-induced shifts in $m$ vs $T_g$ for systems shown in legend, with filled and open symbols denoting values obtained by computational and extrapolated dynamic conventions, respectively.](image)

75
Figure 4.10: $kT/\langle u^2 \rangle$ for polymer beads vs temperature for all the systems shown in the legend. (top) $K_{\text{polymer}} = 1.5$ (bottom) $K_{\text{polymer}} = 3.0$
where an increase in chain stiffness renders the material to be brittle, associated with decrease in the Young’s modulus of the material.

We have three different polymer matrix with widely different slow and fast dynamics. We now study the effect of oligomer additives of varying stiffness on these three polymer matrix (\( K_{\text{polymer}} = 0.0 \) has already been explored in the previous section). Analogous to previous simulations, we begin with a flexible additive and increase the stiffness of oligomeric diluent (Table 3.2). As shown in Figure 4.8, introduction of diluents with stiffness greater than the backbone stiffness of the polymer causes an enhancement in \( \tau_\alpha \) where as the less stiff diluents causes an opposite effect. On the contrary, Figure 4.9 shows that, we can achieve and enhancement in \( T_g \) alone with increase in the diluent stiffness and fragility for these cases remains suppressed relative to the unfilled polymer matrix. A similar observation was not found in Figure 4.1(b) where see an enhancement in fragility for relatively stiffer diluents. From this we conclude that it’s not the absolute stiffness of the diluents that play a crucial role in determining the glass formation behavior of the host polymer, rather it is the relative stiffness of the polymer matrix and diluent.

![Figure 4.11](image.png)

Figure 4.11: \( \Delta H_\alpha \) (red circles) and \( \Delta S_\alpha \) (blue squares) vs oligomer stiffness.
We now focus on the effect of varying stiffness of oligomer diluents on the fast dynamics of semi flexible polymer matrix. Figure 4.10 shows similar trends as in the case of a flexible polymer matrix. All the oligomeric diluents used for semi flexible polymers, shown an enhancement in the modules of the material at all temperature relative to unfilled polymer. We also observe that, analogous to the trends found in case of flexible polymer matrix, we see a cross over in the diluent effect on fast dynamics, where at high temperatures, the most flexible diluent causes a modest increase in the modulus of the host polymer matrix, but at lower temperature, below $T_g$, it shows maximum glassy modulus. This is further be analyzed by looking at $\Delta H_a$ and $\Delta S_a$ behavior amongst these diluents as.

Figure 4.12: GLM collapse of all the simulations involving semi flexible polymers/varying oligomer diluent blends via equation 4.5; (inset) $\alpha$ from the GLM vs oligomer stiffness for $K_{\text{polymer}} = 1.5$ (top inset) and $K_{\text{polymer}} = 3.0$ (bottom inset)
predicted by equation 4.6. Figure 4.11 shows that for flexible diluents yield a favorable \( \Delta S_a \) for the high frequency relaxation compared to stiff additives leading to better molecular packing, which yields higher \( \Delta H_a \).

Similar to what we have seen in the case of flexible polymer matrix, the results shown above for the effect of diluent on the fast and slow dynamics of the host polymer matrix do not track with each other. For a semi-flexible polymer matrix, we see an enhancement in modulus being accompanied by either suppression or enhancement in \( T_g \). But the breadth of glass formation (fragility, \( m \)) is always suppressed relative to unfilled polymer. To further understand the interrelations between fast and slow dynamics, we employ 1-parameter form of Generalized Localization Model (GLM)\(^\text{135} \) to see neat collapse (Figure 4.12) of \( \tau_a \) vs. \( <u^2> \) data with the use of only one adjustable parameter \( a \) (described in previous section).

4.2.3 Effect of varying cross interaction parameter

We now consider the effect of varying cross interaction parameter between the polymer matrix and oligomer diluents. We take a very basic case of flexible polymer and use three different additive stiffness to vary the interaction parameters as shown in methodology section (Table 3.3). We begin by characterizing these diluent induced effects by looking at the impact they have on the slow dynamics of the host polymer. From Figure 4.13 we observe that for a stiff diluent, we always see and enhancement in \( \tau_a \) with increase in interaction strength between the host polymer and oligomer diluent, and as we decrease the stiffness of the diluent, we see this trend to vanish and for a completely flexible additive, we see that only diluent with attractive interaction tend to enhance \( \tau_a \) and diluents with
repulsive interaction tend to suppress \( \tau_\alpha \). This can be also be seen in Figure 4.14, where for stiff diluent we always see an enhancement in \( T_g \) with a crossover in fragility from slight

![Graphs showing \( \tau_\alpha \) vs. temperature for systems with different values of \( K_{\text{additive}} \).](image)

Figure 4.13: \( \tau_\alpha \) vs. temperature for systems shown in the legend. ‘Pure’ refers to unfilled completely flexible polymer.
suppression to enhancement as we increase the interaction strength between polymer and oligomer diluent. But, for a flexible diluent, we see a cross over from suppression in $T_g$ to enhancement while fragility always remains suppressed. Semi flexible diluent ($K_{\text{additive}} = 25.0$) falls in the transition between flexible and stiff diluent.

We also look the effect of varying the interaction strength, on the fast dynamics of the host polymer. From Figure 4.15 we observe that, from stiff and semi flexible diluents, we see and enhancement in modules at all temperatures for entire range of interaction strengths studies here. But in the case of completely flexible diluent, we see for a very low interaction strength between polymer and diluent, we see an opposite effect, similar to *antiplasticization* as seen in the case of small molecule diluent.
Figure 4.15: $kT/\langle u^2 \rangle$ for polymer beads vs temperature for all the systems shown in the legend. ‘Pure’ refers to unfilled completely flexible polymer.
Finally, we look at the interrelations between the effect of varying interaction strength on slow and fast dynamics of a flexible host polymer. Figure 4.16 shows that for all the simulated systems for this study, all collapse on to a single line with $\alpha$ being the only adjustable parameter.

![Graph](Image)

Figure 4.16: GLM collapse of all the simulations carried out by varying cross interaction parameter between diluent and host polymer matrix. (inset) shows the values of $\alpha$ from GLM fits for $K_{\text{additive}} = 100.0$ (red circles); $K_{\text{additive}} = 25.0$ (green circles); and $K_{\text{additive}} = 0.0$ (blue circles);

4.2.4 Universality of the functional form shown in equation 4.2

We have previously shown using equation 4.2 that the Tg shifts caused by an additive can be quantified based upon the high frequency modules, $G_\infty$ (measure of local modulus of the material, $kT/\langle u^2 \rangle$). We have shown for set of polymer/diluent blends where
Figure 4.17: Test of equation 4.2 for the systems (top) where for a given $K_{\text{polymer}}$, a range of oligomer diluents of varying stiffness were used (bottom) where for flexible polymer matrix 3 diluent of varying stiffness were added and within each diluent $\epsilon_{\text{cross}}$ was varied.
the host polymer matrix was completely flexible and the interaction between polymer and
diluent was similar to as between polymer-polymer and diluent-diluent. We now examine
equation 4.2 across all the simulated systems described in previous two sections. We see
from Figure 4.17 that this equation holds well within each set of polymer/diluents blends,
i.e. where polymer matrix is the same and stiffness of the diluent is varied. This is not
universal across all the simulated systems. It also works well within systems where
polymer and diluent are help the same and the interaction strength between the diluent and
the polymer matrix is varied. So, this leads us to further dwell into understanding the
physics of these systems and look further into universal set of parameters which would
scale these the sets of polymer/diluent blends onto a universal curve.

To do so, we draw motivation from the locally correlated lattice (LCL) model
developed by Jane Lipson et al.\textsuperscript{117,118}. They found that the percent free volume at $T_g$ of a
polymer, increases linearly with the experimentally measured $T_g$. This means that there
should be a minimum amount of free volume accessible to the polymer in order to access
melt state. Since it is very difficult to measure the free volume of a polymer directly, we
extend the understanding from GLM model to consider $\langle u^2 \rangle$ of polymer as an estimate to
measure free volume. The onset of caging occurs at about $T_A$, so we can define a quantity
($\langle u^2 \rangle/ u^2_A$) to be ‘percent free volume’ in the glass formation regime. Now using this new
definition of free volume, we plot fractional free volume vs. measured $T_g$ (computational)
for each of our simulated systems. We see in Figure 4.18 that this leads to a linear
correlation ($R^2 = 0.82$) as observed in the work of Jane Lipson et. al.\textsuperscript{117}.
We see in Figure 4.18 that the y-axis is non-dimensional where the x-axis has units of temperature. In an attempt to further generalize this plot we rescale the x-axis by $T_A$ of respective systems. We see from Figure 4.19 that this leads to a much better collapse ($R^2 = 0.94$) as compared to the one in Figure 4.18.

4.2.5 Effect of concentration of oligomer diluent

We study the effect of varying the concentration of diluent on the glass transition behavior of the host polymer matrix. We pick a flexible polymer modified with the stiffest diluent we use ($K_{\text{additive}} = 100.0$) and vary $\epsilon_{\text{cross}}$ (0.6 → 1.4) and concentration of diluent (1%, 3% and 5% by volume). From Figure 4.20 (top) we see that with increase in the interaction strength between the polymer and the diluent and with increase in concentration of the diluent, we see a linear increase in $T_g$, similar to the predictions made by GET.
the polymer/diluent system we have considered here, we observe from Figure 4.20 (bottom) that both $T_g$ and fragility are enhanced in all the cases except for the once where diluent is present in low concentration (1% by volume) and have the least interaction strength with the host polymer matrix.

4.3 Conclusions

In summary, these simulations indicate that oligomeric diluents of varying molecular stiffness can induce diverse alterations in polymer dynamics and mechanical properties. The dependence of $T_g$ on diluent stiffness is found to obey the same functional form describing the $T_g$-dependence of nanoconfined polymers on the stiffness of a confining interface, suggesting that interface and diluent effects on $T_g$ may be mechanistically related. This implicates diluent $\langle u^2 \rangle$ and $G_\infty$ as key parameters controlling polymer $T_g$, with
providing a design rule for diluent selection. We show that this relation is not universal and holds across systems with one variable. We further show that $<u^2>$ can be used as a measure of local free volume of the material and using this definition of $<u^2>$, leads to a universal collapse of the data for in a ‘fractional free volume’ vs. scaled $T_g$ plot, equation 4.2 providing a design rule for diluent selection. We show that this relation is not universal and holds across systems with one variable. We further show that $<u^2>$ can be used as a measure of local free volume of the material and using this definition of $<u^2>$, leads to a universal collapse of the data for in a ‘fractional free volume’ vs. scaled $T_g$ plot, 

Figure 4.20: (top) For $K_{\text{polymer}} = 0.0$ & $K_{\text{additive}} = 100.0$, variation of $T_g$ with increasing $\epsilon_{\text{cross}}$ and concentration of diluent (bottom) dynamic phase diagram capturing the effect of concentration on $T_g$ and fragility in polymer/diluent blends
where $T_g$ is scaled by the onset temperature of glass formation, $T_A$. We also show that GLM successfully describes the relationship between diluent effects on low- and high-frequency dynamics suggests that diluents decouple these regimes by modifying the local anisotropy or anharmonicity of picosecond-timescale segmental rattling. Several observed trends in these systems also qualitatively accord with predictions of the GET. These successes, together with evidence suggesting that the GET and GLM are compatible\textsuperscript{135}, suggest that these models can play an important role in design of diluents with targeted effects on polymer dynamics.
5.1 Introduction

Beginning in the 1990’s, numerous studies have reported alterations in the glass transition temperature $T_g$ of glass-forming liquids under nanoconfinement$^{1-11}$, as measured via ellipsometry and calorimetry. These effects are observed in polymer thin films, small-molecule liquids confined to pores$^{4,6}$, colloids$^{12}$, multi-nanolayered films$^{13,14}$, and polymer nanocomposites$^{15-19}$. They are accompanied by measurements of alterations in other properties including modulus$^{20-22}$ and chain diffusion rates$^{23}$ under nanoconfinement. Recent evidence$^{11}$ suggests that the same effects play an important role in the behavior of ionomers$^{24,25}$, semi-crystalline polymers, and block copolymers$^{26-28}$, making them ubiquitous contributors to the behavior of modern materials. These effects have most commonly been attributed to the presence of long-ranged gradients in dynamics and $T_g$ reported in the vicinity of interfaces in these materials$^{17,29-34,9,35-37}$. This would appear to represent a finding of extreme scientific and technological relevance: it has been suggested that these shifts provide a window into underlying scales of
supercooled liquids, and they are implicated in determining material properties in applications from membranes to microelectronics.

However, this conclusion has been complicated by work reporting that $T_g$, when measured by dynamic methods such as dielectric spectroscopy, frequently exhibits much weaker shifts under nanoconfinement than is observed via pseudo-thermodynamic measurements. This apparent discrepancy has raised questions of whether nanoconfinement and interfaces indeed impose long-ranged alterations in the dynamics of glass-forming liquids. Attempts to explain it have included suggestions of inadequate film annealing, solvent contamination, differences in effective timescale, flaws in data analysis, and the proposition that the pseudo-thermodynamic $T_g$ is entirely decoupled from underlying dynamics under nanoconfinement due to free volume diffusion effects.

Recently, we and others have suggested that other apparent discrepancies in the behavior of nanoconfined materials as probed by distinct metrologies and predicted by computation can be resolved by considering differences in the ways in which these methods probe or average over near-interface gradients in dynamics. Examples include differences between ellipsometry and Debye-Waller factor measurements from neutron scattering, differences in the apparent range of the dynamic interface as determined via different experimental and computational methods, and differences between florescence and ellipsometric measurements. Most recently, the Elastically Collective Nonlinear Langevin Equation Theory for glass formation has been shown to lead to distinct predictions for the values of dynamic and thermodynamic $T_g$’s in freestanding thin films, consistent with the observation of Lipson and Milner that mean film $T_g$’s may not reflect a “democratic” sampling of local dynamics. Here we consider the question of whether a
difference in weightings over an interfacial $T_g$ gradient can account for apparent discrepancies between dynamic and pseudo-thermodynamic measures of $T_g$ in nanoconfined materials in a general manner, without the assumption of any particular model for film dynamics, and without resort to the proposed experimental anomalies or novel mechanisms described above.

We begin by verifying that these apparently discrepant findings can be observed in a single system, in the absence of confounding factors such as solvent contamination. To do so, we perform molecular dynamics simulations of glass formation in bulk and freestanding-film geometries of a linear, unentangled bead-spring polymer based on the model of Kremer and Grest\textsuperscript{182}. Simulation and analysis methods used are explained in detail in Chapter 3.

5.2. Simulation results

Structural relaxation time is determined based on decay in self-part of intermediate scattering function (Chapter 3). Approximate experimental-timescale fragilities of glass formation (shown, for example, in Figure 5.1) are determined for these models based upon an extrapolation of the fit of relaxation time data to the VFT form. Specifically, we evaluate the value of the kinetic fragility index, $m$, at a timescale of $10^{14}$ $\tau_{LJ}$, approximately equivalent to 100s conventional time scale of experimental glass formation (shown in Figure 5.1).

In each system, we compute $T_g$ via several dynamic and pseudo-thermodynamic approaches, illustrated in Figure 5.2 for standard Kremer-Grest bead spring polymer, that have been employed in simulation studies\textsuperscript{161,235} to reflect experimental $T_g$ conventions. A
‘computational timescale’ dynamic $T_g^C$, is defined as the temperature at which $\tau_\alpha$ goes to $10^3 \tau_{LJ}$ (the LJ time unit), the timescale at which our simulations begin to fall from equilibrium. An ‘extrapolated experimental timescale’ dynamic $T_g^E$, is defined as the temperature at which these data extrapolate to $10^{14} \tau_{LJ}$ (approximately 100 s), based upon a fit of in-equilibrium data to the Vogel-Fulcher Tammann relation$^{114,115}$. Finally, dilatometric and calorimetric pseudo-thermodynamic $T_g$’s are defined as the temperatures at which linear fits to the liquid and glassy regimes intersect for the system volume and energy, respectively.

Figure 5.1: Extrapolated bulk state fragility index $m^E$, computed based on a Vogel-Fulcher-Tammann extrapolation to the experimental timescale of the glass transition, vs bond length.
As shown in Figure 5.3, thin film pseudo-thermodynamic $T_g$'s consistently exhibit a greater suppression relative to bulk than do dynamic $T_g$'s; the mean dynamic $T_g$ of the four systems is suppressed by 5% while the mean ellipsometric $T_g$ is suppressed by 15% and calorimetric by 14%. Experimental anomalies, such as solvent contamination and
residual stresses from film spinning, are evidently not needed to observe large differences between nanoconfinement-induced shifts in dynamic and pseudo-thermodynamic $T_g$’s.

5.3 Discussion

This section presents the detailed discussion on the relationship between dynamic and pseudo-thermodynamic measures of $T_g$ in nanostructured materials.

![Figure 5.3: $T_g$ suppression relative to bulk, based on extrapolated dynamic (orange circles), computational dynamic (blue squares), dilatometric (green diamonds), and calorimetric (red triangles) conventions, as a function of bulk fragility computed as in Figure 5.1, with error bars in corresponding colors.](image)

5.3.1 Dependence of $T_g$ gradient weighting on metrology

We now turn to the question of whether this difference between dynamic and pseudo-thermodynamic glass transition temperatures can be explained by a difference in the intrinsic sensitivity of dynamic and pseudo-thermodynamic measures of $T_g$ to different parts of a local gradient in dynamics near the interface. Rather than considering experimental details of specific measurements, we focus on the underlying difference...
between pseudo-thermodynamic and dynamic measures of film $T_g$: the former report the mean value of a pseudo-thermodynamic property, while the latter report a mean relaxation time. We compare the averages reported by these classes of measurement to a linear arithmetic mean over the local values of $T_g$, given by

$$
\langle T_g \rangle = \frac{\int_{-\infty}^{\infty} \rho(z) T_g(z) dz}{\int_{-\infty}^{\infty} \rho(z) dz} \quad 5.1
$$

where $\rho(z)$ is the mean density in a plane parallel to the film at a position $(z)$, $T_g(z)$ is the local average $T_g$ within this plane, and brackets denote a film average. An assumption of this mean has underpinned decades of nanoconfined $T_g$ interpretation\textsuperscript{41,226}.

Consistent with Figure 5.2, pseudo-thermodynamic determinations of $T_g$ commonly employ a two-line construction, wherein the temperature-dependence of a film-average thermodynamic property $X$ is fit to separate linear functional forms well above and well below $T_g$:

$$
\langle X_i \rangle = \langle A_i \rangle T + \langle B_i \rangle \quad 5.2
$$

where $i$ becomes $l$ or $g$ to denote properties in the liquid or glass state, respectively, and $A_i$ and $B_i$ are parameters quantifying the slope and intercept of the corresponding linear fits. The measured pseudo-thermodynamic glass transition temperature $\langle T_g \rangle_{pt}$ is then given by the equation

$$
\langle T_g \rangle_{pt} = \left( \frac{\langle B_l \rangle - \langle B_g \rangle}{\langle A_l \rangle - \langle A_g \rangle} \right)
\left( \langle A_l \rangle - \langle A_g \rangle \right) \quad 5.3
$$
How should this be expected to average over an interfacial gradient in $T_g$? For simplicity, we focus on an average over a single interface at position $z = 0$ between an empty half-space in the negative $z$ and the material in the positive $z$. If we consider any temperature well above or below the mean $T_g$, the film average value of $X$ (density, in dilatometry, or extensive energy, in calorimetry) is given by

$$\langle X_i \rangle = \lim_{b \to \infty} \frac{1}{b} \int_0^b X_i(z) \, dz$$

By definition, the relationship provided by equation 5.2 applies both to film average or local in-film properties. Making use of this fact gives

$$\langle A_i \rangle = \lim_{b \to \infty} \frac{1}{b} \int_0^b A_i(z) \, dz \quad \text{and} \quad \langle B_i \rangle = \lim_{b \to \infty} \frac{1}{b} \int_0^b B_i(z) \, dz$$

Combining equations 5.3 and 5.5 yields

$$\langle T_s \rangle_{pt} = \lim_{b \to \infty} \frac{\int_0^b \left( B_x(z) - B_i(z) \right) \, dz}{\int_0^b \left( A_i(z) - A_x(z) \right) \, dz}$$

Applying equation 5.3 to local dynamics in the film gives

$$\langle T_s \rangle_{pt} = \lim_{b \to \infty} \int_0^b T_s(z) w_{pt}(z) \, dz$$

where $w_{pt}$ is a weighting function with the properties of a probability distribution function, given by
Equation 5.8 is the key result of the above development: the mean film $T_g$ determined via any pseudo-thermodynamic method is a film average of local $T_g$’s, weighted by the local difference between the liquid and glass-state temperature derivative of the corresponding thermodynamic variable. This difference is often larger near a free surface, where $T_g$ is suppressed, than in the film center or near an attractive substrate (for example, see Figure 5.4), such that pseudo-thermodynamic methods will generally yield a $T_g$ that is weighted towards lower-$T_g$ regions of the film.

Should we then conclude that differences between dynamic and pseudo-thermodynamic measurements of $T_g$ in nanoconfined systems emerge purely from the
weighting of pseudo-thermodynamic $T_g$ measurements? To answer this question, we consider how *dynamic* measurements average over the film. These measurements probe a mean relaxation time $<\tau_a>$, which is nonlinearly related to $T_g$ and will therefore yield a differently weighted average:

$$
\langle \tau_a \rangle = \frac{\int_{-\infty}^{\infty} \rho(z) \tau(z) dz}{\int_{-\infty}^{\infty} \rho(z) dz}
$$

5.9

To relate this to a mean inferred $T_g$, we require a form for the relationship between $\tau_a$ and $T$. For a sufficiently narrow window around the glass transition, the temperature dependence of $\tau_a$ can be reasonably-well described by an effective Arrhenius temperature dependence,

$$
\tau(z) = \tau_0(z) \exp\left[\frac{E_a(z)}{(kT)}\right]
$$

5.10

where $E_a$ is an effective activation energy given by

$$
E_a = k \frac{d \ln \tau}{d (1/T)}
$$

5.11

Applying this equation at $T_g$ gives

$$
E_a = kT_g \ln \frac{\tau_g}{\tau_0}
$$

5.12

where $\tau_g$ is the fixed relaxation time conventionally defining the location of the dynamic $T_g$ (commonly 100 s) and $\tau_0$ is an adjustable parameter not to be equated with the genuine high-temperature relaxation time. Taking the above equations to hold locally at any plane
in the film with position dependent parameters $T_g(z)$ and $\tau_0(z)$, and substituting back into equation 5.9 then yields

$$\langle \tau \rangle = \int_{-\infty}^{\infty} \rho(z) \tau_0(z) \exp \left[ \frac{T_g(z)}{T} \ln \frac{\tau_g}{\tau_0(z)} \right] dz \quad 5.13$$

which provides an equation for the mean film relaxation time in terms of local $T_g$'s. In order to obtain an equation for the mean film $T_g$ as determined via a dynamic measurement, we consider the application of equation 5.12 to film average relaxation behavior and rearrange to give

$$\langle T_g \rangle_d = \langle E_a \rangle \left( k \ln \frac{\tau_g}{\langle \tau_0 \rangle} \right) \quad 5.14$$

Because the Arrhenius relations employed to obtain these equations are defined at $T_g$ rather than at high temperature, local Arrhenius parameters can be related to the local temperature-dependent fragility of glass formation $m(z)$, defined as

$$m(z) = \frac{d \log \tau(z)}{d(T_g(z)/T)} = \frac{1}{T_g(z) \ln 10} \frac{E_a(z)}{k} = \frac{1}{\ln 10} \ln \frac{\tau_g}{\tau_0(z)} \quad 5.15$$

Making use of the last of these equalities, while employing equation 5.11 at the level of the mean-film relaxation time to determine $\langle E_a \rangle$, and with equation 5.13 providing the film-mean relaxation time, then leads to

$$\langle T_g \rangle_d = \left[ \int_{-\infty}^{\infty} T_g(z) \frac{m(z)}{\langle m \rangle} f(z) \right]_{\tau=T_g} \quad 5.16$$

where
And where we have neglected the temperature-derivative of the local density for simplicity.

Here $f(z)$ is again a weighting function with the properties of a probability distribution function, and $<m>$ is the mean film fragility, which averages over the dynamic gradient in a manner we have previously shown\textsuperscript{237}. Equations 5.16 and 5.17 indicate that the mean film $T_g$ determined via dynamics is weighted towards regions of the film with higher $T_g$ and higher fragility.

These derivations indicate that mean dynamic measures of $T_g$ are weighted towards the slower-relaxing parts of nanostructured materials, whereas mean pseudothermodynamic measurements of $T_g$ are weighted towards the faster-relaxing parts of these materials. For this reason, mean dynamic $T_g$’s will tend to be higher than corresponding pseudo-thermodynamic $T_g$’s under nanoconfinement. Given the large fraction of studies focusing on systems exhibiting suppressed $T_g$ under nanoconfinement, it is to be expected that an apparently weaker $T_g$-nanoconfinement effect would commonly be observed by dynamic methods. We note that this explanation does not require any difference in the underlying gradient of dynamics probed by these methods.

5.3.2 Test of $T_g$ weighting in simulations

If this reasoning is correct, then performing the averages given by equations 5.6 and 5.16 over a local dynamic $T_g$ gradient calculated for these simulations should yield inferred mean film $T_g$’s in closer agreement with the pseudothermodynamic and dynamic
overall film \( T_g \)’s. To perform this test, we first determine the segmental relaxation time on a layer-by-layer basis as described in the methods section. We then determine \( T_g^c \) for each layer via the same approach employed for the overall film. The resulting \( T_g \) gradients are shown in Figure 5.5(a) and (b). As in prior simulation studies, these systems exhibit a smooth suppression in \( T_g \) upon approach to the free surface. We note that since this gradient is calculated dynamically from bins of discrete thickness, it already incorporates a portion of the dynamic weighting. Use of equations 5.6 and 5.16 will therefore still tend to yield results somewhat biased towards the (higher) mean dynamic \( T_g \). An exceptionally high spatial resolution gradient would eliminate this issue but is prohibited by poor statistical sampling in very small bins.

As shown by Figure 5.5(c), a simple density-weighted discrete numerical average over this gradient yields a mean film \( T_g \) that is intermediate between the mean film dynamic and pseudothermodynamic values, consistent with the weighting arguments above. If we instead average over this gradient employing the dynamic weighting given by equation 5.17, the inferred dynamic film \( T_g \) becomes considerably higher (increasing to a \( \sim 3\% \) reduction relative to bulk), consistent with the above arguments. On the other hand, applying the pseudothermodynamic weighting given by equation 5.7 shifts the gradient-average \( T_g \) towards the mean-film pseudothermodynamic \( T_g \), decreasing to a \( \sim 10\% \) reduction relative to bulk. As discussed above, the ‘overshoot’ relative to the mean dynamic \( T_g \) measurement and ‘undershoot’ relative to the mean film pseudothermodynamic \( T_g \) result from the fact that these discrete gradients already contain some dynamic weighting.
Figure 5.5: (a) gradients in computational dynamic $T_g$ (b) gradients in extrapolated dynamic $T_g$ for systems with bond length 0.96 (blue), 0.88 (red), 0.83 (green), and 0.79 (purple). (c) $T_g$ suppression vs. bulk fragility via the same convention (open circles), computed via two line fit to change in thickness (open squares), computed via a linear average over the local values of $T_g$ in the interfacial gradient (solid triangles), computed using the pseudo-thermodynamic weighting factor in eq.5.7 (solid diamonds) and using the dynamic weighting factor provided by eq. 5.16 (solid circles).
This analysis indicates that simply considering these different weightings can account for very large differences in $T_g$ shifts under nanoconfinement as probed by dynamics vs pseudo-thermodynamics. This reinforces the proposition that the difference between the two measurement classes is a matter of weighting over a common gradient rather than a difference in the underlying physics probed.

While this simulation test was performed in freestanding films, one can expect the same weighting considerations to apply in supported films as well. The surface gradient in such films is widely understood to be comparable to surfaces on freestanding films. On the other hand, if the substrate is sufficiently rigid and attractive, a gradient towards slower dynamics will then emerge at the substrate, as has been seen in prior experimental and simulation work\textsuperscript{31,174,207}. The above weighting equations indicate that such a regime will be overrepresented in the dynamic average; an expected corresponding reduction in liquid state thermal susceptibilities will lead to an underrepresentation of this region in thermodynamic measures of $T_g$. In essence, the quantity $T_g / T_{g,\text{bulk}}$ will remain larger when measured by dynamic than by thermodynamic methods. Thus, in scenarios in which the mean film $T_g$ drops under nanoconfinement in supported films (as in a large fraction of experimental studies of nanoconfinement), the effect will appear to be ‘larger’ when measured by thermodynamic rather than dynamic methods.

5.4 Conclusions

In summary, while we cannot exclude a role for experimental artifacts in specific measurement studies, we show that these issues are not necessary to account for a general finding of weaker suppressions of $T_g$ under nanoconfinement as probed by dynamic than pseudo-thermodynamic methods. Moreover, measurements via both methods are
intimately connected to the underlying film dynamics: each reflects a differently weighted average over local gradients in these dynamics, with pseudothermodynamic methods weighted towards low- $T_g$ regions and dynamic methods weighted towards high- $T_g$ regions. There is no way either weighting can yield a non-bulk-like $T_g$ in the absence of an underlying gradient in $T_g$, since all other quantities involved in the average enter via weighting functions that integrate to one. This finding suggests that the majority of extant data are consistent with the presence of long-ranged interfacial gradients in segmental dynamics and glass formation behavior.

Neither instrument details nor any model of the form of interfacial gradients are necessary to arrive at these conclusions; rather they emerge simply from the fact that dynamic measurements fundamentally report a mean relaxation time while pseudothermodynamic measurements report a mean pseudo-thermodynamic property. Ultimately, the two values provide high (dynamic) and low (pseudothermodynamic) bounds to a linearly weighted mean film $T_g$, with instrument-specific weightings potentially playing a role in addition to these generic effects\textsuperscript{232}. In our companion paper, we additionally illustrate that, moving beyond nanoconfinement effects on single systems, these metrology-dependent weighting effects can confound observed trends in the strength of nanoconfinement effects from system to system. Future work should therefore employ pseudo-thermodynamic and dynamic methods as complementary probes of nanoconfinement effects on segmental dynamics and the glass transition.
CHAPTER VI

DOES FRAGILITY OF GLASS FORMATION DETERMINE THE STRENGTH
OF $T_g$-NANOCONFINEMENT EFFECTS?

6.1 Introduction

Alteration in the glass transition behavior of polymers and other soft materials upon confinement induces pronounced changes in glass transition temperature $T_g$ [194–199], modulus [212,213], and diffusion rates [215], and can impact material performance, for example by leading to unanticipated mechanical failure of nanostructured materials [238]. Such nanoconfinement effects are observed in a broad range of materials, including polymers, small-molecule glass-formers [197,199], and colloids [205]. Understanding these effects and their dependence on interfacial and bulk material properties has therefore been the focus of a substantial body of work over several decades [14,19,23,31,32,194,197,212,215,231,239–245] and has been the subject of multiple reviews [196,198–200,202,204,246,247].

It has commonly been anticipated that these nanoconfinement effects on $T_g$ should be sensitive to the rate at which liquid dynamics slows down near $T_g$ upon cooling, a property known as the “fragility” of glass formation. Understanding the effect of fragility on the glass transitions of nanoconfined polymers would provide a useful design rule for nanostructured materials. For example, one of the major adverse impacts of
nanoconfinement is a softening of nanostructures relative to the corresponding bulk state of their constituent polymer. There is some evidence that these effects can be minimized by use of low-fragility materials or fragility-reducing additives, providing a potential route to the formulation of robust nanostructures. However, the universality of correlations between bulk fragility of glass formation and the strength of $T_g$-nanoconfinement effects remains unsettled. Moreover, in our companion paper, we demonstrate that the method of determining $T_g$—via a dynamic or thermodynamic convention—can substantially alter the magnitude of measured $T_g$ shifts from bulk by changing the manner in which the measurement averages over local gradients in dynamics. This raises the question of whether apparent correlations between $T_g$ and fragility are robust with respect to the choice of $T_g$ metrology. Here we employ molecular dynamics simulations of glass formation in polymer thin films to address these issues.

There are at least two plausible mechanisms by which the strength of nanoconfinement effects might be expected to scale with the bulk fragility of glass formation. First, although the fragility of glass formation most directly quantifies the susceptibility of liquid dynamics to thermal perturbation, it is intuitively reasonable that it should correlate with the susceptibility of dynamics to other perturbations, such as introduction of a free surface. The theoretical prediction that fragility more intrinsically reflects underlying aspects of configurational entropy, rather than simply an empirical temperature dependence, strengthens this expectation.

Second, the Adam-Gibbs (AG) theory of glass formation is commonly viewed as implying a correlation between fragility and the scale of cooperatively rearranging regions (CRRs) that are hypothesized to enable propagation of interfacial dynamic
perturbations into the interior of confined materials. Specifically, the AG theory rationalizes the non-Arrhenius temperature dependence of $\tau_\alpha$ in fragile glass-forming liquids as resulting from the growth of a cooperative length-scale of dynamics:

$$\tau = \tau_\infty \exp \left( \frac{L}{L_A} \cdot \frac{\Delta \mu}{k_B T} \right)$$  \hspace{1cm} (6.1)

where $L$ is the number of cooperating units in a CRR, $L_A$ is the value of this quantity at the onset temperature $T_A$ of glass formation, $\Delta \mu$ is the high-temperature free energy of segmental relaxation, $\tau_\infty$ is a high temperature relaxation time, $k_B$ is Boltzmann’s constant, and $T$ is temperature.

This viewpoint is often interpreted as indicating that liquids with more cooperative dynamics should exhibit greater deviations from Arrhenius behavior (i.e. lower fragilities). Within this interpretation, less fragile liquids are expected to exhibit smaller CRRs, a correspondingly reduced range over which dynamics are altered near an interface, and therefore lower susceptibility to interfacially-driven nanoconfinement effects. Moreover, a number of studies have suggested that finite size effects – modification of the material’s behavior due to truncation of underlying correlation lengths – may also play an important role in nanoconfinement effects. Within this perspective, the dynamics higher-fragility systems should be characterized by larger-scale cooperative rearrangements and therefore should be more susceptible to finite-size-related nanoconfinement effects.

Several pieces of evidence support a correlation between fragility and the strength of nanoconfinement effects. In a simulation study, Riggleman et al. reduced the fragility of glass formation of a bead-spring polymer via introduction of an antiplasticizer additive and
found that this nearly eliminated the $T_g$ reduction observed in the corresponding pure polymer film$^{252}$. Similar effects have been observed experimentally upon introduction of small-molecule diluents that, among other things, reduce the fragility of glass formation$^{14,238}$. More recently, Evans et al. examined $T_g$ reductions relative to bulk in a series of supported polymer films of varying fragility, and they found that $T_g/T_g^{\text{bulk}}$ increased monotonically towards unity with decreasing fragility of glass formation$^{253}$. They interpreted this trend in terms of a decreasing length scale of nanoconfinement effects, presumably in accordance with the second potential mechanism discussed above.

In these studies, fragility was varied by altering composition, either by introducing an additive or by simply selecting a different polymer. As a consequence, it is difficult to draw firm conclusions regarding the generality and magnitude of the observed dependence of confinement effects on fragility, as factors such as chain chemistry, composition gradients, and so on may play a role, distinct from fragility, in influencing the strength of nanoconfinement effects. Indeed, interfacial composition gradients were directly observed in Riggleman et al.’s study$^{15}$, raising the possibility that a difference in the chemical nature of the interface may have contributed to results. The antiplasticizer additives employed in that study$^{15}$ also alter dynamic and mechanical properties in a variety of ways$^{4,73,94,248}$ that may or may not directly relate to fragility changes but that may play a role in determining confinement effects. Finally, as noted above and in our companion paper, experimental evidence and theory suggest that the method of determining $T_g$ may impact the magnitude of observed nanoconfinement effects$^{175,226-232}$. It is presently unsettled whether the choice of $T_g$ convention can play any role in observations of a correlation between the strength of $T_g$ nanoconfinement effects and fragility.
In addition to these issues, several studies have reported results that raise questions regarding the relationship between fragility and the strength of nanoconfinement effects. First, Shavit et al. found that a series of simulated polymer films of varying chain backbone stiffness exhibited a reduction in nanoconfinement effects with increasing stiffness, which also correlates with increased fragility\(^{254}\). However, this deviation from the expected fragility dependence of nanoconfined \(T_g\) was attributed to enhanced surface ordering with increasing chain stiffness, such that the generality of this finding remains unclear. Moreover, the evidence for a correlation between the CRR size and the strength of \(T_g\) nanoconfinement effects is somewhat ambiguous\(^{40,255}\). Even more broadly, a number of studies have raised questions regarding strength of the proposed correlation between fragility and the scale of CRRs \(^{256–258}\) – a core element of the hypothesis described above. Additional studies on the relationship between fragility and nanoconfined \(T_g\) in which potentially confounding factors are minimized or accounted for would therefore be of great value.

In order to isolate the impact of fragility on \(T_g\)-nanoconfinement from other confounding variables, we perform molecular dynamics simulations of two series of bead-spring polymer films in which the bulk fragility of glass formation is systematically varied \textit{via} two distinct routes (Chapter 3). In the first series of simulations, bulk fragility is reduced by reducing the bond length of the chain backbone; in the second series, both \(T_g\) and fragility are varied via the introduction of several molecular diluents based on prior work quantifying the effect of these diluents on bulk glass formation behavior\(^{235}\).
6.2 Results and discussion

This section presents the detailed discussion on the influence of polymer fragility on the strength of Tg-nanoconfinement in nanostructured materials.

6.2.1 Bulk behavior of polymer systems

We begin by quantifying the bulk glass formation behavior of the model systems described above to provide a basis for assessing the dependence of nanoconfinement effects on bulk fragility. As shown in Figure 6.1, these models probe an appreciable range

![Figure 6.1: Segmental relaxation time $\tau_\alpha$ vs temperature for bulk simulations of the models described in the manuscript. Blue symbols correspond to pure polymers with chain backbone length (BL) noted in the legend. Red symbols correspond to polymer/oligomer blends with oligomer backbone stiffness noted in the legend. Grey symbols correspond to the polymer/monomer blend. Solid symbols in red and grey represent bulk systems with 5% diluent concentration and hollow symbols represent the same systems but with the modified normalizing bulk diluent concentration shown in Table 6.1](image-url)
of relaxation behavior. As shown in Figure 6.2, shortening the model’s backbone bond length reduces the bulk $T_g$ modestly and $m$ substantially. Consistent with prior work$^{235,252}$, introduction of the single-bead additive reduces both $m$ and $T_g$ substantially. Polymerizing this additive to form an oligomer substantially weakens the $T_g$-suppression effect, while

Figure 6.2: Bulk state values $m$ and $T_g$ for the systems in this study normalized by their values in the standard Kremer-Grest polymer described in the text, via (a) computational convention and (b) extrapolated convention. Symbols have the same meaning as in Figure 6.1.
retaining an overall suppression in $T_g$ and $m$ relative to the neat polymer. Introducing moderate stiffness to the oligomer yields a mixture with enhanced $T_g$ but suppressed $m$ relative to the neat state, whereas a very stiff oligomer enhances both $T_g$ and $m$ relative to the neat polymer. Introducing moderate stiffness to the oligomer yields a mixture with enhanced $T_g$ but suppressed $m$ relative to the neat state, whereas a very stiff oligomer enhances both $T_g$ and $m$ relative to the neat polymer.

Figure 6.3: Computational versus extrapolated values of $T_g$ (a) and kinetic fragility index (b). Lines are linear fits to the data enhanced $T_g$ but suppressed $m$ relative to the neat state, whereas a very stiff oligomer enhances both $T_g$ and $m$ relative to the neat polymer. These trends are consistent whether one considers computational or extrapolated conventions for $T_g$ and $m$; as shown by Figure 6.3, values determined from the two conventions are well-correlated for both $m$ and $T_g$ (the coefficient of determination $R^2$ for a linear relationship between values obtained via the two conventions is 0.98 for $T_g$ and 0.97 for $m$). By including systems in which $T_g$ and $m$
are altered from the standard KG model in these diverse manners, study of the effect of nanoconfinement on these systems should allow deconvolution of the dependence of \( T_g \)-nanoconfinement effects on \( m \) and \( T_g \) as tuned via diluent introduction vs. other methods.

6.2.2 Film Thickness

In comparing the glass transition behavior of multiple nanoconfined polymers, it is essential to retain a constant film thickness so that comparison is not confounded by thickness-driven differences in the magnitude of the nanoconfinement effect. Because both backbone bond length alterations and introduction of diluents alter the polymer’s density, we vary the number of chains in each thin film simulation, as shown in Table 6.1, (while holding the cross-sectional area constant) in order to maintain a nearly constant film thickness.

![Figure 6.4: Comparison of thickness of all simulated systems as a function of temperature. Symbols have the same meaning as in Figure 6.1](image-url)
thickness. As shown in Figure 6.4, this successfully produces films that are within 1 sigma thickness of each other over the entire temperature range of interest.

6.2.3 Test of fragility hypothesis

The strength of nanoconfinement effects on the glass transition is commonly quantified by the ratio $T_g/T_g^{bulk}$. In systems exhibiting a $T_g$-reduction (such as freestanding films), lower values of this ratio signify a greater nanoconfinement effect on the glass transition. The recent work by Evans et.al.\textsuperscript{253} reports a dependence of $T_g/T_g^{bulk}$, measured via pseudothermodynamic methods (differential scanning calorimetry in the bulk and fluorescence intensity measurements in thin films), on bulk fragility ($m_{bulk}$), with higher bulk fragilities predicting a greater nanoconfinement effect. The strength of the dependence of $T_g/T_g^{bulk}$ on fragility appears to be highest at high fragility, although it is not clear whether the data can, within uncertainty, support any particular functional form beyond a roughly linear reduction in the strength of the nanoconfinement effect with decreasing fragility. Here we ask whether a similar trend is observed in these simulated systems. We begin by considering the $T_g$ inferred from the overall film dynamics and comparing this to the bulk value of $T_g$ by the same convention for each polymer or polymer/diluent blend. As shown by Figure 6.5, one might infer a modest correlation between $m$ and $T_g/T_g^{bulk}$ if one focused only on the pure polymer systems in which fragility is varied via an alteration in bond length ($R^2$ for a linear relationship between $m$ and $T_g/T_g^{bulk}$ for these systems only is 0.66 for extrapolated $T_g$ and $m$ values and 0.64 for computational $T_g$ and $m$ values). The blends of a polymer with a monomer or flexible oligomer also appear to be consistent with this trend ($R^2$ increases to 0.82 and 0.77 for extrapolated and computational values, respectively, with addition of these points). However, once the systems with stiffer
oligomeric additives are introduced to the data set, the net correlation between fragility and $T_g/T_{g,bulk}$ disappears ($R^2$ drops to 0.0 via both computational and extrapolated conventions).

Figure 6.5: Nanoconfinement effect as determined by $T_g/T_{g,bulk}$ plotted vs. bulk fragility for (a) computational (b) extrapolated cutoffs. Symbols have the same meaning as in Figure 6.1.

Figure 6.6: Nanoconfinement effect as determined by $T_g/T_{g,bulk}$ vs. bulk $T_g$. Symbols have the same meaning as in Figure 6.1.

Recently, it has also been suggested that higher $T_g$ polymers may be more susceptible to nanoconfinement effects\textsuperscript{259}. In order to consider this alternate possibility of a correlation between the strength of $T_g$ nanoconfinement effects and bulk $T_g$, we also plot in
Figure 6.6 the correlation between $T_g/T_{g,bulk}$ and bulk $T_g$. At least at this level, there appears to be a stronger correlation between $T_g/T_{g,bulk}$ and bulk $T_g$ than between the former quantity and fragility ($R^2$ for a for a linear relationship between $T_g/T_{g,bulk}$ and $T_g$ for this complete set of systems is 0.51 for computational values and 0.74 for extrapolated values).

Should these data be interpreted as indicating a lack of correlation between $T_g$ nanoconfinement effects and $m$ and indicating an appreciable correlation with bulk $T_g$, or as suggesting that the two systems containing stiff oligomers are in some way outliers? To answer this question, we now consider two possible confounding factors within these simulations that are also potential confounding factors within experimental studies of this trend: the possibility that $T_g$ data for films comprised of polymer/additive blends may be confounded by the presence of concentration gradients; and the question of whether different choices of $T_g$ metrology may yield different apparent results.

6.2.4 Effect of concentration gradients

Table 6.1: Modified diluent concentration used to account for film-center concentration changes in polymer/diluent blend thin films

<table>
<thead>
<tr>
<th>Stiffness of diluent (K)</th>
<th>Diluent volume percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>100.0</td>
<td>5.81</td>
</tr>
<tr>
<td>5.0</td>
<td>5.99</td>
</tr>
<tr>
<td>0.0</td>
<td>6.09</td>
</tr>
<tr>
<td>Single Bead</td>
<td>5.68</td>
</tr>
</tbody>
</table>

First, we test whether composition gradient effects in the diluent-modified polymers may play a role in these systems’ behavior. As shown by Figure 6.7, thin films
of these systems exhibit two related compositional features. First the diluent concentration tends to be depleted near the free surface, with this effect more pronounced in the oligomeric diluent blends than the monomeric diluent blends. Second, this surface depletion leads to an enhancement, relative to bulk, in diluent concentration throughout the film central region. This leads to a significant enhancement in $\tau_\alpha$ in the center of the film compared to bulk values in the nominally comparable system at the same overall mole fraction of the additive, shown for the $K = 100$ additive in Figure 6.7b. This is not the result of a nanoconfinement effect per se; rather it simply results an enhanced mid-film concentration of a relaxation-suppressing additive. This raises the possibility that much of these systems’ apparent deviation from the nanoconfinement/fragility correlation may result from an enhancement of the mid-film additive concentration rather than from a true dynamics-nanoconfinement effect. Perhaps comparing to a bulk diluent concentration equal to that in the center of each film would yield better agreement with the expected fragility/$T_g$-suppression correlation.

To test this possibility, we conduct a new set of simulations of bulk-state polymer/diluent blends in which the diluent concentration is selected to match the mid-film diluent concentration in each thin film system, as shown in Table 6.1. As shown by the hollow points in Figure 6.5, this renormalization slightly weakens these systems’ deviations from the expected correlation but by no means eliminates them ($R^2$ is 0.09 and 0.0 via computational and extrapolated conventions respectively). Evidently, even data
Figure 6.7: (a): Mole fraction of diluent as function of distance $Z$ from the interface at $T = 0.58$. The solid line indicates the mean (29%) mole fraction. (b) and (c): $\tau_\alpha / \tau_{\alpha,\text{bulk}}$ vs. $T$ plotted at a range of distances from the film surface for the polymer film containing the $K = 100$ oligomeric additive, with the normalizing relaxation time determined from the (b) standard 5\% by volume bulk simulation and (c) modified 5.81\% by volume bulk simulation.
accounting for this composition gradient effect still do not exhibit a universal correlation between $T_g/T_{g,\text{bulk}}$ defined via this convention and fragility. On the other hand, as shown by Figure 6.6, performing this correction for shifts in mid-film diluent concentration essentially eliminates the previously appreciable correlation between $T_g/T_{g,\text{bulk}}$ and bulk $T_g$ ($R^2$ with renormalized mid-film concentrations is 0.01 for computational values and 0.03 for extrapolated values). Evidently, this correlation was entirely a result of trends in mid-film diluent concentration and therefore was not representative of a trend in true $T_g$-nanoconfinement effects.

These results emphasize the possibility that experimentally observed trends in nanoconfined $T_g$ involving blends may involve a considerable influence of composition gradient effects. It is generally recognized that additives may confound these trends by altering interfacial energies, which play an important role in $T_g$-nanoconfinement\(^{207,240}\), and can thereby confound the observation of pure dynamic nanoconfinement effects. The present results suggest a second possible route by which compositional gradients may play a role: if the bulk $T_g$ depends nonlinearly on gradient composition (which is often the case), then alterations in mid-film concentration relative to bulk may lead to $T_g$ shifts that have an intrinsically bulk rather than interfacial origin.

Are these composition gradient effects the only confounding factor contributing to these results? To answer this question, for the remainder of the paper, we focus on understanding the relationship between nanoconfined $T_g$ and fragility once these composition-gradient effects have been accounted for via the above renormalization.
6.2.5 Role of $T_g$-metrology

In Chapter V, we demonstrate that $T_g$ as determined from mean film dynamics does not report, as one might expect, a linear arithmetic average of near-interface gradients in $T_g$. Instead, the mean film $T_g$ reported by dynamic measurements such as those employed here includes a weighting factor that leads to apparent average $T_g$'s that are higher than the linear arithmetic average. A similar weighting effect occurs in pseudothermodynamic measurements of mean films $T_g$, albeit with the bias typically in the other direction. Is it possible that observed trends in $T_g$ with fragility, both here and in experiment, are confounded by alterations in these weighting factors between systems?

To test this, we compute $T_g$ in each system as a function of distance from the interface so as to provide a basis for quantifying changes in near-interface $T_g$ in the absence of potentially confounding weighting factors. As can be seen in Figure 6.8, $T_g$ is locally suppressed near the film free surface and gradually returns to a bulk value at distances far from the interface, when the normalizing bulk composition for polymer/additive blends is given by the film-center concentration as described above (Table 6.1). As described in our companion paper, an unweighted $T_g$ can be extracted by performing a linear arithmetic average over these $T_g$ gradient data. For clarity, we refer to this linear arithmetic average $T_g$ as $T_{g,LAA}$. As shown in Figure 6.9, $T_{g,LAA}$ exhibits a stronger correlation with fragility than the mean-film $T_g$, provided that midfilm composition changes relative to bulk are also accounted for as described in the prior section ($R^2$ for a linear relationship between $T_{g,LAA}$ and $m$ for all systems, when $T_{g,bulk}$ is based on the composition in Table 6.1, is 0.43 for computational $T_g$ and $m$ values and 0.67 for extrapolated $T_g$ and $m$ values).
Figure 6.8: $T_g/T_{g,\text{bulk}}$ plotted as a function of distance from the interface, with (a) the bulk $T_g$ for polymer/additive blends based on the bulk concentrations shown in Table 6.1 and (b) the bulk $T_g$ for polymer/additive blends based on the standard 5% volume fraction described in the methods section. Symbols have the same meaning as in Figure 6.1.

Figure 6.9: Nanoconfinement effect as determined by $T_g/T_{g,\text{bulk}}$, with $T_g$ determined via a linear arithmetic average over the gradient data shown in Figure 6.8, vs. bulk fragility (a & b) and vs. bulk $T_g$ (c & d). Symbols have the same meaning as in Figure 6.1.
Apparently the weighting effects on $T_g$ determined from mean-film dynamics are not uniform between all of these systems. As shown in Figure 6.10, not only is the value obtained from the mean film $T_g$ generally biased upward relative to the linear arithmetic average, but the two measures of $T_g$ are not well correlated ($R^2 = 0.08$). Particularly significant deviations between the two are seen in the polymer/additive blends. In this case, eliminating these non-uniform weighting effects by employing a linear arithmetic average over the $T_g$ gradient reveals a weak to modest correlation between fragility and nanoconfined $T_g$.

Figure 6.10: Comparison between the mean film $T_g$ and linear arithmetic average $T_g$. Symbols have the same meaning as in Table 6.1.

Evidently, not only can metrological weighting effects lead to a shift in nanoconfined $T_g$ as described in our companion paper, but they can also qualitatively alter apparent trends in the strength of $T_g$-nanoconfinement effects from system to system. Given that many of the studies in the literature employ a single $T_g$-metrology, this raises the possibility that weighting effects may play a role in apparent systematic trends. These
results emphasize the importance of combining multiple metrologies in confirming proposed relationships between $T_g$ and other quantities under nanoconfinement.

6.2.6 Physical origins of fragility effects

The prior sections indicate that, even once all identified confounding factors are accounted for, changes in fragility account for only about half of the variation in $T_g/T_g_{, \text{bulk}}$ between systems. Moreover, the magnitude of this dependence also is somewhat weak—an extrapolation of a linear fit to the composition-corrected linear-arithmetic-average values $T_{g, \text{LAA}}/T_{g, \text{bulk}}$ shown in Figure 6.8 suggests that a system with $m = 16$ (perfectly Arrhenius) would still exhibit a 2\% $T_g$ reduction. For a polymer with bulk $T_g$ of 373K, for example, this would correspond to a reduction of more than 7 K. The residual reduction at low fragility inferred from computational $T_g$ values is even larger.

Given the reasoning presented in the introduction, how can we explain the statistically-weak and low-magnitude nature of the correlation between fragility and $T_g$ nanoconfinement effects observed here? To answer this question, we consider one-by-one the following core postulates of the cooperativity hypothesis described in the introduction that appears to link fragility to the strength of $T_g$-nanoconfinement effects:

1) The distance $\xi_s$ over which surface-induced alterations in segmental dynamics penetrate into the film is determined by the scale $L$ of cooperatively rearranging regions (CRRs), proposed by Adam and Gibbs$^{249}$.

2) The size of CRRs (and therefore the range $\xi_s$ of interfacial dynamic perturbations) is determined by fragility, as is often inferred from the Adam-Gibbs theory.
The magnitude of $T_g$ alterations in a thin film geometry is predominantly determined by the range over which dynamic perturbations penetrate into the material relative to the overall material thickness.

6.2.6.1 Does cooperative motion set the interfacial dynamic gradient scale?

First, we consider whether our data are consistent with postulate 1, suggesting that $\xi$ is determined by the scale of CRRs. A number of prior simulation studies have indicated that this is indeed the case\cite{175,225}. In a prior work, one of the present authors suggested that the hypothesis of a proportionality between $\xi$ and the average number of segments $L$ in a CRR can be tested by checking whether the Adam-Gibbs equation (equation 6.1) holds if $\xi$ is substituted for $L$ in that equation to yield\cite{175}

$$\tau = \tau_\infty \exp \left( \frac{\xi \Delta \mu}{\xi_{\tau,A} k_B T} \right)$$

6.2

This approach has the advantage of not involving any assumptions about the form of the CRRs – it is a general test of the proposition that $\xi$ is proportional to the CRR size and therefore should satisfy the AG relation. To test this in the present simulations, we first determine $\xi$ for each system as a function of temperature by computing $\tau_\alpha$ as a function of distance from the interface and then defining $\xi$ as the distance from the interface at which $\tau_\alpha$ returns to 80% of its bulk value (employing a 4th-degree polynomial for data smoothing and interpolation). This method is consistent with a number of prior works\cite{174,175,216}.

As shown by Figure 6.11(a), the resulting values of $\xi$ grow on cooling, consistent with prior work\cite{34,37,38,155,175,216,223}. The constant $\xi_{\tau,A}$ is determined for each system by determining $\xi$ at the onset temperature of glass formation $T_A$, which is defined, consistent
with prior work, as the first temperature upon cooling at which $\tau_\alpha$ deviates by 10% from an extrapolated Arrhenius fit to high-temperature data. $\tau_\infty$ is treated as an adjustable shift parameter. As in prior work, $\Delta \mu$ is a high temperature activation free energy, $\Delta \mu = \Delta H - T \Delta S$ (where $\Delta H$ and $\Delta S$ are the high temperature activation enthalpy and entropy, respectively). $\Delta H$ and $\Delta S$ are specifically determined as in prior work based on a fit to high-temperature relaxation time data$^{260}$.

Figure 6.11: (a) Length scale, $\xi$, defined as the distance from interface where $\tau_\alpha$ returns to 80% of its bulk value (b) $\xi$ as function of temperature normalized by the corresponding $T_g$ of the system. Symbols have the same meaning as in Figure 6.1.

As shown by Figure 6.12, the data indicate that all systems satisfy equation 6.2. This indicates that range of interfacial perturbation to segmental dynamics is indeed proportional to $L$ in these systems, confirming postulate 1) above. Evidently, this component of the hypothesis is not responsible for the weakness of the $T_g/T_{g,bulk}$ vs $m$ correlation.
6.2.6.2 Is the size of the interfacial dynamic gradient determined by fragility?

We now consider part 2) of the hypothesis above. Given that the interfacial dynamic range apparently is proportional to the CRR size, are these two scales then determined by the fragility of glass formation? To test this, we first return to the $\xi_{\tau}/\xi_{\tau,A}, \Delta \mu/T$ data shown in Figure 6.11(a). While these data suggest the presence of substantial differences in these systems’ interfacial dynamic length scale, simply rescaling the temperature axis by the bulk $T_g$ of each system causes all of the data to collapse to a single curve, shown in Figure 6.11(b). Since these systems, by design, do not exhibit a general correlation between bulk $T_g$ and $m$ (see Figure 6.2), this collapse indicates that it is possible to substantially vary fragility without significantly altering $\xi_{\tau}$ beyond the extent already accounted for by changes in $T_g$. Evidently, $m$ is not a universal predictor of $\xi_{\tau}$. Since the prior section indicated that $\xi_{\tau}$ and $L$ are well correlated in these systems, this suggests that $L$ is also not well-correlated with the kinetic fragility index $m$. How can this be reconciled with the
common interpretation of the Adam-Gibbs theory as indicating a fundamental correlation between a non-Arrhenius temperature dependence of dynamics and cooperative motion?

To answer this question, we return to the Adam-Gibbs equation itself and ask what relationship, if any, it rigorously indicates between cooperative motion and relaxation. By combining the Adam-Gibbs equation (equation 6.2) with the definition of the kinetic fragility index (equation 6.1), we obtain

\[ m = \frac{1}{kT_g \ln 10} \frac{L_g}{L_A} \left[ \Delta \mu_L \left( \frac{\partial L/L_g}{\partial T_g/T} \right)_{T=T_g} + \left( \frac{\partial \Delta \mu/T}{\partial 1/T} \right)_{T=T_g} \right] \]

6.3

where \( L_A \) and \( L_g \) are CRR size at \( T_A \) and \( T_g \) respectively. An equation comparable to this was previously demonstrated by Starr et al.\cite{181}. Within this functional form, it appears that the AG theory indeed predicts at least some relationship between \( m \) and CRR size via the prefactor \( L_g/L_A \). However, by applying equation 6.3 in the limit that \( T \) goes to \( T_g \),

\[ \log \frac{\tau_g}{\tau_0} = \frac{L_g}{L_A} \frac{\Delta \mu_g}{kT_g \ln 10} \]

6.4

de this can be reduced to

\[ m = \log \frac{\tau_g}{\tau_0} \left[ \frac{\Delta H}{\Delta \mu_g} + \left( \frac{\partial L/L_g}{\partial T_g/T} \right)_{T=T_g} \right] \]

6.5

The prefactor \( \log(\tau_g/\tau_0) \) is nearly constant for all glass formers, equal to approximately 16 due to the rough universality of high temperature relaxation times and the conventional definition of \( T_g \) as occurring at a relaxation time of 100s. Notably, the absolute value of the CRR size has now been eliminated from the AG expression for fragility: this simplified
version clearly indicates that the kinetic fragility index is determined by the \textit{temperature dependence of scaled CRR size} (\(\frac{\partial L}{L_n}\)) and not by the CRR size itself (\(L\)). Furthermore, \(m\) can be decoupled from even this term via variations in the high-temperature relaxation behavior of the material, as quantified by the first term in equation 6.5, which is not characteristic of the material’s glass formation behavior at all.

The AG theory should therefore not be viewed as predicting a universal relationship between fragility and the scale of cooperativity. In other words, within the AG theory, it is entirely possible for modifications to a polymer’s structure or introduction of diluents to decrease fragility without decreasing the scale of cooperative motion at \(T_g\) (or vice versa). This observation is evidently a central driver of the weak correlation observed in these simulations between \(m\) and the strength of \(T_g\)-nanoconfinement effects, even when other confounding variables are accounted for.

6.2.6.3 Is the magnitude of mean \(T_g\)-nanoconfinement effects controlled by their interfacial range?

It appears that a breakdown in postulate 2) of the hypothesis above portends that there should be a substantial non-universality in any correlation between \(m\) and the strength of \(T_g\) nanoconfinement effects. This is consistent with the breakdown of this correlation observed in these simulation results. We nevertheless consider postulate 3) – the proposition that changes in the magnitude of nanoconfinement effects near free surfaces of different materials are driven largely by variations in the range of interfacial \(T_g\) gradients. Beyond the question of the role of fragility in nanoconfinement effects, this postulate is relevant to the long use of two-layer and three-layer models to model and interpret experimental \(T_g\) measurements in thin films\textsuperscript{194,229}. 

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Returning first to the $T_g$ gradient data in Figure 6.9, we find these gradients are well fit by a decaying exponential form given by

$$
\frac{T_g(z)}{T_{g,\text{bulk}}} = 1 - \left(1 - \frac{T_{g,\text{surface}}}{T_{g,\text{bulk}}} \right) \exp \left(-\frac{z}{\xi_{T_g}}\right)
$$

where $T_{g,\text{surface}}$ is the glass transition temperature directly at the film surface and $\xi_{T_g}$ is a measure of the range over which this interfacial $T_g$-perturbation extends into the film.

Figure 6.13: Length scale in $T_g$ gradients determined by the fit of binned $T_g$ to equation 6.6 as a function of (a) computational fragility (b) $T_g$ suppression plotted vs. this length scale. Symbols have the same meaning as in Figure 6.1.

As shown in Figure 6.13(a), $\xi_{T_g}$ is weakly anticorrelated with fragility ($R^2$ for a linear anticorrelation is 0.29), indicating that more the fragile glass formers among these systems have a weak tendency towards shorter-ranged $T_g$ gradients. This is precisely the opposite of what one would expect if higher fragilities drive larger $T_g$ suppressions via an enhanced interfacial range. Moreover, Figure 6.13(b) indicates that the overall $T_g$ suppression in these films is poorly correlated with $\xi_{T_g}$ ($R^2 = 0.01$).
Why does the range of the $T_g$ gradient fail to predict the strength of the $T_g$-nanoconfinement effect? As shown by Figure 6.14(a), the amplitude $A \equiv 1 - \frac{T_{g,\text{surface}}}{T_{g,\text{bulk}}}$ of near-surface $T_g$ perturbations from bulk also plays an important role. Unlike $\xi_{T_g}$, $A$ is positively correlated with fragility ($R^2 = 0.80$), indicating that more fragile glass formers tend to exhibit a greater amplitude of near-surface perturbations in $T_g$. However, as shown by Figure 6.14 (b), $A$ is still only modestly correlated with the mean $T_g$ reduction ($R^2 = 0.47$). How can this be?

![Figure 6.14: (a) Amplitude $A$ of $T_g$ gradients, determined as a fit parameter for the fit of binned $T_g$ to equation 6.6, vs bulk fragility. (b) $T_g$ suppression vs $A$. Symbols have the same meaning as in Figure 6.1.](image)

To answer this, we formally derive from equation 6.6 the film linear arithmetic average $T_g$ of a film of half-thickness $h$ with a near-surface $T_g$ gradient obeying equation 6.6. This is given by an integral over equation 6.6, yielding

$$\frac{\langle T_g \rangle}{T_{g,\text{bulk}}} = 1 - \frac{\xi_{T_g}}{h} \left( 1 - \frac{T_{g,\text{surface}}}{T_{g,\text{bulk}}} \right) \left( 1 - \exp \left( - \frac{h}{\xi_{T_g}} \right) \right),$$

$$6.7$$
This equation indicates that, for thick films, the $T_g$ suppression will be dominated by the product $A \xi T_g$. As shown by Figure 6.15, this quantity is indeed well-correlated ($R^2 = 0.93$) with the overall $T_g$ suppression in these films.

Figure 6.15: $T_g$ suppression plotted vs the product of amplitude and length scale of $T_g$ gradients as determined from the fit of binned $T_g$ to equation 6.6. Symbols have the same meaning as in Figure 6.1.

These results indicate that the range of the interfacial $T_g$ gradient does not dominate shifts in mean film $T_g$ (even as determined via a linear arithmetic average). Instead, these shifts from system to system can involve trends in both range and magnitude of the interfacial $T_g$ gradient. Why, then, might results from experimental studies tend to emphasize range effects more strongly? To answer this question, we consider the question of how one would infer an interfacial range from these systems given only data accessible experimentally.
In a typical series of thin film experiments, the film-thickness-dependence of mean film $T_g$ is the primary information available. While we have not directly simulated multiple film thicknesses, we can infer this thickness dependence for each system by employing equation 6.7 with the fit to the $z$-dependence of $T_g$ in each of these films. In essence, a measurement of the interfacial gradient of $T_g$ in a single film thickness of a polymeric material enables us to make an estimate of the thickness dependence of mean film $T_g$ in that material. The resulting inferred thickness dependences of $T_g/T_{g,\text{bulk}}$ on film thickness $h$ are shown in Figure 6.16(a). We now analyze these data in two ways consistent with experimental data treatment. In these treatments, we truncate the $h$-dependence at a 10% reduction in $T_g$, as this is consistent with the largest $T_g$ suppressions observed in most experiments due to limitations on the lower bounds of film thickness typically accessible.

Figure 6.16: (a) Scaled average $T_g$ as the function of film thickness as determined from equation 6.7. (b) Collapse of data in part (a) by via a system-dependent renormalization by a parameter $\lambda$.

First, we fit these data via the functional form of Keddie et al\textsuperscript{19},
\[ \frac{T_g(z)}{T_{g,\text{bulk}}} = \left[ 1 - \left( \frac{\xi_{KJ}}{d} \right)^\delta \right] \]

This leads to an inferred interfacial range \( \xi_{KJ} \). As shown in Figure 6.17(a), this is well correlated with \( T_{g,LAA}/T_{g,\text{bulk}} \) (\( R^2 = 0.96 \)). However, as shown in Figure 6.17(b), it is uncorrelated with the genuine range of the underlying \( T_g \) gradient (\( R^2 = 0.0 \)). In other words, a false correlation between \( T_g \) suppression and the interfacial range of \( T_g \) would emerge via this treatment because \( \xi_{KJ} \) convolutes the range and amplitude of near-surface \( T_g \) perturbations. Since there exists a modest correlation between \( T_g \) suppression and bulk \( m \), as discussed above, this would lead to a false inferred correlation between \( m \) and the range of the dynamic interface,

\[ \begin{align*} 
\text{Figure 6.17: Inferred interfacial range } \xi_{KJ} \text{ from equation 6.8 vs. (a) bulk fragility, (b) } \\
T_{g,LAA}/T_{g,\text{bulk}}, \text{ and (c) Genuine range of underlying } T_g \text{ gradients, } \xi_{Tg}. \text{ Symbols have the same meaning as in Figure 6.1.} 
\end{align*} \]
Second, we apply an approach recently employed by Evans et. al.\textsuperscript{253} to infer a correlation between fragility and the interfacial range of $T_g$. Within this approach, one simply finds a length scale $\lambda$ for each system such that a rescaling of $h$ by $\lambda$ leads to a collapse of all the data in Figure 6.16(a). In their paper, they appear to have chosen $\lambda$ such that $T_g$ is suppressed by approximately 2.5% at $h/\lambda = 1$. We follow this protocol, leading to the collapse shown in Figure 6.16(b). As shown in Figure 6.18 the resulting values of $\lambda$ show a strong correlation with $T_{g,LAA}/T_{g,bulk}$ ($R^2 = 0.93$) and a poor correlation with $m^C$ ($R^2$

![Graph](image)

**Figure 6.18:** Length scale $\lambda$ corresponding to 2.5% suppression in $T_g$ as determined from equation 6.7 vs. (a) bulk fragility, (b) $T_{g,LAA}/T_{g,bulk}$, and (c) Genuine range of underlying $T_g$ gradients, $\xi_{Tg}$. Symbols have the same meaning as in Figure 6.1.
Again, however, $\lambda$ is poorly correlated with the genuine underlying range of the interfacial $T_g$ gradient ($R^2 = 0.11$) due to convolution with the magnitude of this gradient.

6.3 Conclusions

It has commonly been anticipated that the bulk fragility of glass formation of a glass-forming liquid should predict its susceptibility to $T_g$-nanoconfinement effects. Based on molecular dynamics simulations of several systematically varied series of polymeric glass-formers, here we find that this correlation is weak and likely non-universal. Results indicate that confounding factors such as composition gradients and variations in measurement weighting over interfacial dynamic gradients have the potential to conceal such correlations or potentially create their appearance where none exist. For example, we find that alterations in mid-film diluent concentration in the mid-film relative to the bulk can generate a correlation between $T_g$ suppression and bulk $T_g$ that is driven by mixing rather than true $T_g$-nanoconfinement effects. While it is possible to deconvolute this from a true nanoconfinement effect in simulation thanks to the availability of nanoscale spatially resolved composition and dynamics data, in experiment this would be very difficult to distinguish from a trend in nanoconfinement effects on $T_g$.

Even once the confounding factors are controlled, fragility is found to have only modest power to predict the magnitude of suppressions in $T_g$ in thin freestanding films compared to the bulk. Why does the expectation of a strong correlation between fragility and $T_g$-nanoconfinement effects fail even once confounding factors are accounted for? While the interfacial dynamic range is found to be controlled by the scale of cooperative rearrangements, neither quantity is well correlated with the fragility of glass formation. This finding is consistent with a reassessment of the predictions of the AG equation to
show that it does not, contrary to common intuition, predict a simple relationship between the sc. Finally, we find that the range of alterations in $T_g$ at the free surface is modestly anticorrelated with fragility within the systems studied here. This effect is dominated by a positive correlation between the magnitude of near-interface $T_g$ shifts to yield an overall modest correlation between fragility and the magnitude of the over film $T_g$ reduction as computed via a linear arithmetic average over the gradient. In other words, any correlation between fragility and the magnitude of nanoconfinement effects on $T_g$ appears to be more closely linked to a change in the amplitude of interfacial shifts in dynamics than to their range. This presents a very different physical picture of any such correlation than one rooted in variations in the scale of cooperative rearrangements. In particular, since a major effect of a free surface is a local modification of the density, this suggests that the component of fragility associated with variations in density may be of greater significant to nanoconfinement than the isochoric fragility. In essence, materials with a higher isothermal fragility may be more sensitive to variations in density at a film surface.

Practically, these results suggest that overall fragility of glass formation is likely to be an unreliable predictor of a material’s susceptibility to $T_g$-nanoconfinement effects. A number of prior studies have indicated that interfacial energy and the softness of the confining material play important roles in determining the magnitude and direction of $T_g$ nanoconfinement effects. Evidence in this study and elsewhere suggest that these factors are not sufficient to fully predict shifts in a material’s $T_g$ under nanoconfinement; different materials additionally appear to exhibit variable susceptibility to these effects. Given that fragility evidently is not sole factor in determining this susceptibility, additional research
is warranted to identify other factors playing a role. It seems likely that multiple factors, potentially including chemically specific structural alterations at the interface, may be involved. The above reasoning specifically suggests that a focus on the density-variation contribution to fragility, excluding the isochoric contribution, may be more fruitful.

More broadly, these results highlight the profound challenges that arise in the metrology of nanostructured materials. For example, we find that common experimental analysis methods have the potential to yield a false correlation between fragility and the inferred range of $T_g$-nanoconfinement effects. These issues can be compounded by basic variations in the manners in which measures of mean film $T_g$ weight over local gradients in dynamics. Together with our companion paper highlighting these metrological issues, these findings highlight the critical importance of combining multiple metrology methods and spanning diverse systems in ongoing efforts to identify structure/property relations describing nanoconfinement effects on the glass transition and related properties.
CHAPTER VII
THREE-LAYER MODEL FOR THE EMERGENCE OF ULTRASTABLE GLASSES FROM THE SURFACES SUPERCOOLED LIQUIDS

7.1 Introduction

The last several years have seen the emergence of a new class of glassy materials – “ultrastable” glasses produced by vapor deposition. These materials exhibit unusual kinetic and thermodynamic stability, with enhanced densities, enhanced moduli\textsuperscript{1,2}, suppressed energies, and increased softening temperatures. Estimates suggest that these enhancements would require tens to thousands of years to obtain via a typical temperature quench into the glass state. Due to these extraordinary properties and speculation that they may closely approach a posited “ideal glass” state\textsuperscript{3,4}, these materials have been the focus of great attention\textsuperscript{2,3,5–8}.

Experimental and simulation\textsuperscript{9,10} studies have attributed ultrastable glass properties to the presence of a surface layer of enhanced mobility. This view is commensurate with long-standing ‘two-layer’ models for the surface behavior of glass-forming liquids, wherein a thin layer of enhanced mobility can be found immediately at the surface before giving way to bulk-like material\textsuperscript{11}. This mobile surface layer is posited to allow access to configurations lower on the material’s potential energy landscape, enabling access to
higher densities and lower energies than are accessible via normal melt quenches\textsuperscript{55,268,269}. However, the precise mechanism by which this surface mobility is translated into high-stability glasses remains unsettled.

In particular, the enhancement in glassy density found in ultrastable glasses is not consistent with some of the most influential models of enhanced surface mobility during glass formation, which view the shift in near-surface dynamics as directly emerging from an enhancement in local free (or specific) volume\textsuperscript{200,222,270} or segmental rattle space\textsuperscript{271,272} near the interface. These perspectives are conceptually similar to the idea of the surface layer as possessing an enhanced “rheological temperature” relative to the bulk. For example, the Doolittle formulation of free volume theory suggests that

\[
\tau = \tau_0 \exp \left[ \frac{qv_0}{v - v_0} \right]
\]

where \(\tau\) is segmental relaxation time, \(\tau_0\) and \(q\) are constants, \(v_0\) is some minimal occupied or excluded volume, and \(v\) is the specific volume. Within free volume perspective of near-surface dynamics, this (or some other similar) relationship is expected to hold for dynamics near the free surface, with the enhanced mobility simply reflecting a reduced local density. Since these models preserve the bulk state relationship between relaxation time and density or free volume, they suggest that enhanced surface mobility should not lead to an enhanced glass-state density at lower temperature. We therefore highlight two key open questions regarding the origin of ultrastable glasses:

1) Why does the surface region of enhanced stability allow access to higher densities, rather than simply freezing in the bulk glassy density at a lower temperature?
2) Do these materials leverage an already-existing region of enhanced density present at the surfaces of quiescent glassy films, or are the high densities and stabilities found in these materials created by the deposition process itself?

Here we suggest a more detailed mechanistic understanding of the origin of the extraordinarily high thermodynamic and kinetic stabilities observed in ultrastable glasses. This understanding indicates that a layer of enhanced glass-state density exists near the surface of *quiescent* liquids as a result of a mismatch in the range over which thermodynamic properties and mobility are altered near a free surface in supercooled liquids, as described below. This mismatch allows the system to locally circumvent the usual relationship between density and mobility to achieve glass-state densities greater than bulk. The observation of this layer of enhanced density at the surface of a model quiescent film supports the view that vapor deposition processes leverage the equilibrium behavior of surfaces in supercooled liquids and that deposition-specific effects, such as induced molecular orientation\(^ {273,274}\), are not the central mechanism driving the high stabilities of these materials.

7.2 Proposed model

Several decades of evidence suggest that \(T_g\) and segmental relaxation time vary over a range on the order of 10 nm or more near the surface of many glass-forming liquids\(^ {196-198,200,203,204,246,267,275}\). Evidence to this effect includes shifts in overall film \(T_g\), direct observations of gradients in the glass transition temperature\(^ {218,276,277}\) and relaxation dynamics\(^ {278,279}\), and predictions of long-range gradients from computer simulation\(^ {175,222,280}\). By contrast, gradients in density \(\rho\) at liquid/gas interfaces far from the vapor-liquid critical point are generally much shorter-ranged, on the order of 1 nm\(^ {175,222}\).
An apparently unrecognized implication of this mismatch in dynamic and thermodynamic interfacial length scales, reflecting a breakdown of the free-volume-layer view\textsuperscript{222}, is that the standard two-layer model of film dynamics outlined above is inadequate to describe the surfaces of supercooled liquids. Instead, such a material is minimally divided into three layers, as shown in Figure 7.1: a layer immediately at the surface with suppressed $T_g$ and liquid-state $\rho_l$, a layer far from the interface possessing bulk $T_g$ and liquid-state $\rho_l$, and an additional intermediate layer with bulk-like liquid-state $\rho$ but suppressed $T_g$. We denote this the “facilitated” layer, because, as discussed below, its liquid-state dynamics are facilitated by proximity to the free surface without it exhibiting a corresponding density suppression. This facilitated layer has a unique property that is critical to the understanding of ultra-stable glasses produced by vapor deposition. In the liquid state, the facilitated layer essentially follows the bulk-state density equation of state. However, its $T_g$ is lower than that in the bulk. Therefore, at temperatures below the bulk

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**Figure 7.1:** Schematic of three-layer model for near-free-surface dynamics in glass-forming liquids, as described in the text. $\rho_l$ and $\rho_g$ denote liquid- and glass-state densities, respectively.
$T_g$, the density of this layer will continue to increase according to the liquid-state thermal expansion coefficient, while the bulk thermal expansion coefficient drops to its glassy value. This naturally leads to a higher density in this region than in the bulk, with the density enhancement given by

$$\rho(T) - \rho_b(T) = \left( \frac{\partial \rho}{\partial T} \bigg|_{\text{liquid}} - \frac{\partial \rho}{\partial T} \bigg|_{\text{glass}} \right) \left[ T_g^f - T_g^b \right]$$  \hspace{1cm} (7.2)

where $T_g^f$ is a mean $T_g$ of the facilitated layer. This enhancement in density will naturally be tracked by a reduction in energy following an analogous equation in the specific heat, consistent with observations in ultrastable glasses. This view is consistent with recent experimental work indicating that vapor-deposited glasses modestly below $T_g$ indeed exhibit thermodynamic properties consistent with the supercooled liquid state\textsuperscript{281,282}.

7.3 Comparison to simulation

To illustrate this effect more clearly, we employ data from previously published simulations of a freestanding film of a linear bead-spring polymer\textsuperscript{237}. The methodological details of this simulation can be found in reference\textsuperscript{237}. In summary, the simulations consist of an approximately 20 nm thick film (employing a common conversion of one Lennard-Jones (LJ) distance unit to approximately one nm\textsuperscript{201,283,284}) of unentangled polymer chains, subject to a quench towards the glassy state. In order to test the three layer model proposed above, we quantify dynamic and structural properties of the film as a function of distance from the interface, defined as the point in the surface density gradient at which the density is half that at the center of the film.
Figure 7.2: Mean density (solid lines, averaged across two interfaces each for 4 trials) as a function of temperature for regions 0.875 LJ distance units thick, at positions $z$ from the interface, located in the surface layer, intermediate layer, and bulk layer of the simulated free interface. Points denote the $\rho$ data point closest to the glass transition temperature of each region (with a resolution of 0.02 in LJ temperature units). The dashed lines are extrapolations of this data from the glass transition temperature of each region, following the temperature dependence of density in the bulk glass.

As illustrated by Figure 7.2, the system behaves as expected in the equilibrium liquid state: the surface layer exhibits a strong suppression in density, while the facilitated layer exhibits density essentially equal to the bulk layer. However, $T_g$ in the facilitated layer, defined for these simulations based on a common convention as the temperature at which the simulations begin to fall out of equilibrium on a timescale of $10^3$ LJ time units, exhibits
a suppression from bulk. For this reason, the facilitated layer continues to increase in density after the bulk has fallen into the glassy state. We can assess the implications of this for the glass-state density by assuming that the glass-state density follows the bulk glass-state temperature dependence (local density data in the glassy state tends to be...
overwhelmed by noise in simulations of this size). As shown by this figure, this naturally leads to an enhanced glass-state density, relative to bulk, of the facilitated layer.

This outcome is emphasized by Figure 7.3 (rendered in part using the Visual Molecular Dynamics Software Package\textsuperscript{285}), which compares spatially-resolved near-surface gradients in three properties: the local anomaly from bulk of

\[
T_g \left( \frac{T_g(z)}{T_{g,bulk}} - 1 \right),
\]

the local anomaly from bulk of density at a fixed temperature in the liquid state

\[
\left( \frac{\rho(z, T = 1.35T_{g,bulk})}{\rho_{bulk}(T = 1.35T_{g,bulk})} - 1 \right)
\]

and the anomaly of the local density at the local \(T_g\) as compared to that of the bulk system at its \(T_g\)

\[
\left( \frac{\rho(z, T = T_g(z))}{\rho_{bulk}(T = T_{g,bulk})} - 1 \right).
\]

This figure confirms the three-layer picture illustrated schematically in Figure 7.1. The facilitated layer exhibits nearly bulk-like density in the liquid state combined with a suppressed \(T_g\), leading to a peak density enhancement of 1.5% at the layer \(T_g\) relative to the bulk density at the bulk \(T_g\). Notably, the magnitude of this density enhancement is consistent with that observed in experimental ultra-stable glasses\textsuperscript{268}. In these simulations, the breadth of this layer is of order 4 nm. Prior work has indicated that the range of the dynamic gradient driving this region continues to grow on further cooling, with extrapolations to the experimental-timescale \(T_g\) suggesting a thickness on the order of 10 nm\textsuperscript{175}. A thickness in this range of order four to ten nm is generally consistent with experimental measurements of the range of near-interface gradients in \(T_g\) and near-\(T_g\) dynamics\textsuperscript{221,276}.

The key properties of ultra-stable glasses can therefore be explained by a model in which vapor-deposition methods grow the facilitated layer in a layer-by-layer fashion
without exposing it to high enough temperatures to perturb its anomalously high-density glassy state. Once this layer is buried in the bulk, it will exhibit a fictive temperature of roughly $T_g^{f}$ – the $T_g$ of the facilitated domain. Calculations of the equivalent quench or annealing time will then indicate that the material corresponds to a bulk glass formed via a temperature quench to yield $T_g = T_g^{f}$. Measurements of $T_g$ in highly confined materials suggest that $T_g$ in this domain can be suppressed by up to 50K to 80K in many cases, making reports of fictive temperature suppressions of 30K or more (and corresponding equivalent aging times in the tens to thousands of years) in ultrastable glasses quite consistent with this mechanism.

Finally, we note that this more detailed mechanism is also qualitatively consistent with the experimentally observed temperature and rate dependences of ultra-stable glass formation, wherein excessively high rates of vapor deposition fail to produce ultra-stable glasses and the optimum temperature for deposition is commonly found to be several tens of Kelvin below the bulk $T_g$. Specifically, previous work has found that the dynamic gradient that is central to this model becomes smaller at high rates of quench into the glassy state. Since the effective thermal quench rate of the deposited material depends on the temperature of the substrate and the deposition rate, excessively low deposition temperatures or high deposition rates likely probe an effective high-quench-rate regime in which the facilitated layer disappears. Conversely, excessively high substrate temperatures do not fully leverage the $T_g$ difference between the bulk and facilitated layers, effectively reducing the temperature difference in equation 7.3 and thereby muting the magnitude of the overall effect. This model suggests, in fact, that the optimum deposition temperature should be near the $T_g$ of the facilitated layer, since lower temperatures will
rapidly vitrify the facilitated layer without benefiting from any further-liquid like densification. Evidence on the $T_g$ of this layer is sparse, but experiments in very thin polymer films suggest that a $T_g$ suppression of order 50K is likely in this region. This is reasonably consistent with experimental optimum temperatures of deposition on the order of 15% below $T_g$. For example, in the case of trinaphthylbenzene, the optimum deposition temperature is reported to be near $T_g - 50K$, relative to a bulk $T_g$ of 347K.

7.4 Conclusions

We have proposed and tested versus simulation an expanded three-layer model for the surfaces of supercooled liquids. This model suggests that the following answers to the open questions highlighted above regarding the origin of ultrastable glasses produced by vapor deposition.

Why does the surface region of enhanced stability allow access to higher densities, rather than simply freezing in the bulk glassy density a lower temperature? This model suggests that interfacial mobility enhancement is a necessary but not sufficient condition for achieving ultra-stable glasses. A surface mobility gradient that simply reflected a local density (as in free-volume models of near-surface dynamics) would indeed yield a lower local $T_g$ without enhancing the glass-state density, consistent with the ‘enhanced rheological temperature’ picture that has sometimes been presented for supercooled liquid surfaces in the literature. The key ingredient in circumventing this very general density/mobility coupling (which is a key underpinning of the common success of free volume theories of glass formation in bulk polymers) is the presence of a nanoscale ‘facilitated’ region in which mobility is enhanced but density is essentially bulk-like. From this perspective, the very existence of ultra-stable glasses produced by vapor deposition
may provide a new piece of evidence supporting the existence of long-ranged gradients in dynamics at the surfaces of glass-forming liquids, corresponding to a local failure of free-volume relationships between density and mobility.

*Do these materials leverage an already-existing region of enhanced stability present in ultra-stable glasses, or are the high densities and stabilities found in these materials created by the deposition process itself?* These simulation data and reasoning suggest that an enhancement in density, suppression in energy, and enhancement in kinetic stability consistent with ultrastable glasses can emerge as a natural consequence of an equilibrium phenomenon – a mismatch in the range of thermodynamic and dynamic gradients at free surfaces of quiescent supercooled liquids. While deposition-specific effects such as induced molecular orientation may play a role in the details of a given ultra-stable glass, these details are evidently not necessary to realize the enhanced kinetic and thermodynamic stability that most essentially characterize ultra-stable glasses in general. This finding is consistent with prior simulation\textsuperscript{288} and experimental\textsuperscript{273,274,289} work finding that ultra-stable glass formation does not universally correlate with formation of a particular anisotropic molecular orientation. If correct, these findings also suggest that an enhancement in density and reduction in specific energy consistent with those observed in ultrastable glasses should be present in very thin (order 10 nm or less) freestanding films well below their $T_g$. Metrology of such thin films remains a major challenge; however, these results suggest that these types of measurements could be of considerable value in providing new understanding of near-interface dynamics in supercooled liquids.

These findings naturally raise an additional question: how can the facilitated layer exhibit bulk-like density but dramatically accelerated dynamics? Previously published
evidence suggests that surface mobility enhancements may propagate into the material beyond the surface density gradient via cooperative rearrangements that are predicted by the theory of Adam and Gibbs\textsuperscript{249} to universally underpin dynamics in non-Arrhenius supercooled liquids\textsuperscript{175,204,216,225}. Recent simulation results in model systems comparable to the one considered here have provided strong evidence for this picture, indicating that the range of the dynamic interface is linearly related to the size of these cooperatively rearranging regions\textsuperscript{175,204,216,225}. In this view, dynamic cooperativity enables the facilitated layer to benefit from the mobility of the free surface well beyond the range of the surface density suppressions. A similar conclusion (albeit grounded in a very different physical model) is suggested by the recently developed elastically collective nonlinear Langevin equation theory for dynamics in thin films, which suggests that the absence of an elastic medium beyond the film surfaces lowers a long-ranged elastic barrier to collective relaxation over a range exceeding that of interfacial density alterations\textsuperscript{233,290}. The present results indicate that the decoupling of local density/mobility relationships suggested by both of these theories can account for the high densities and stabilities realized in ultrastable glasses. Viewed another way, these results indicate that the realization of ultrastable glasses by vapor deposition should be interpreted as a new piece of evidence for the presence of medium-ranged dynamic correlations\textsuperscript{249} in supercooled liquids.
CHAPTER VIII
OVERALL SUMMARY AND FUTURE STUDIES

The broad objective of this research was to develop an understanding between the parallels that exist between the underlying physics of glass formation in polymer/diluent blends and nanostructured materials. We showed that diluent induced changes in polymer’s glass transition temperature, \( T_g \), can be predicted based on the diluent’s Debye-Waller factor \(<u^2>\), a measure of it’s high-frequency shear modulus. The exact functional form is analogous to the one suggested in literature for predicing \( T_g \)-shifts in nanostructure materials. Further, we developed a more universal relation which predicts the changes in polymer’s \( T_g \) due to a diluent based on a free volume approach developed by Jane Lipson et al.\textsuperscript{117}. Success of the GLM in describing the relationship between diluent effects on low- and high-frequency dynamics suggests that diluents decouple these regimes by modifying the local anisotropy or anharmonicity of picosecond-time scale segmental rattling. Several observed trends in these systems also qualitatively accord with predictions of the GET. These successes, together with evidence suggesting that the GET and GLM are compatible, suggest that these models can play an important role in design of diluents with targeted effects on polymer dynamics.
In general there are many open question in the field studying the effect of diluents on glass formation behavior and mechanical properties of the host polymer as well as in the field studying nanostructured materials. In addition, introduction of diluents to nanostructured materials further complicates the problem. Through Chapters I and II we laid down the current understanding developed in the above-mentioned field of study and poise specify questions we wish to answer in this dissertation. In Chapter III, we elaborately talked about the generic models we use to carry out the simulations and also summarized all the simulations carried out in order to answer our questions. We also talked about the analysis techniques used in this study.

In Chapter V, we sorted out the apparent discrepancies between pseudo-thermodynamic and dynamic measurements of $T_g$-nanoconfinement effects that have raised questions regarding the presence of long-ranged interfacial dynamic gradients in glass-forming liquids. Here we showed that these differences can be accounted for based on disparities in these methods’ weightings over local $T_g$’s within an interfacial gradient. This finding suggests that most experimental data are consistent with a broad interfacial dynamic interphase in glass-forming liquids.

In chapter VI, we took inspiration from previous work which suggested interrelations between nanoconfinement effects, cooperative dynamics in supercooled liquids, and the fragility of the glass transition. It is commonly expected that nanoconfinement effects on $T_g$ should be more pronounced for more fragile glass formers. Here, we systematically tuned fragility via several routes. Results indicate that a correlation between fragility and the strength of nanoconfinement effects is weak to modest at best when considering all systems, but can appear to be stronger when considering a subset of
systems. This outcome is consistent with a reanalysis of the Adam-Gibbs theory of glass formation indicating that fragility does not necessarily track in a universal way with the scale of cooperative motion in glass-forming liquids. Finally, we find that factors such as composition gradients or variability in measurement sensitivity to different parts of the dynamic gradient have the potential to significantly confound efforts to identify trends in $T_g$-nanoconfinement effects with variables such as fragility, emphasizing the importance of employing large data sets and multiple metrologies in the study of this problem.

Finally, in Chapter VII we showed that enhanced densities and stabilities consistent with ultrastable glasses specifically can emerge as a result of a mismatch in the length scales of thermodynamic and dynamic gradients at the surfaces of equilibrium supercooled liquids. In particular, ultrastable glass properties can be understood within a three-layer model of the interface in which a “facilitated layer” intermediate between the surface and bulk exhibits bulk-like liquid-state density but suppressed $T_g$. This mismatch in length-scale has previously been correlated with the scale of cooperative rearrangements in the supercooled state. This suggests that ultrastable glasses may be a direct consequence of the cooperative nature of dynamics in equilibrium supercooled liquids.

The Following are some recommendations for future work:

- The data reported in this dissertation can be useful for testing emerging glass transition theories.
- In this work, by adding molecular diluents to bulk polymer and nanostructured materials, we alter bulk state fragility and the dynamic length scales associated with thin nanoconfined materials. Previous work by Riggleman et al.\textsuperscript{291} has shown that these
alterations have similarities associated with ageing behavior. In this light, it would be interesting to study how the addition of molecular diluents alters the ageing behavior of the polymer in bulk and under confinement.

- Polymer thin films have a wide range of applications that are listed in detail in the background section of this dissertation. Here it becomes important for these materials to have mechanical robustness. A simulation study followed by experimental validation can be set up for understanding the impact of diluents of mechanical robustness of the polymer thin film.

- We have showed different weighting factors associated with dynamics and pseudo-thermodynamics measures of $T_g$ of confined materials. A neat experimental study can be designed for a simple system like polystyrene where $T_g$ is measured via all the existing experimental techniques and use our weighting factors to account for the differences arising due to metrological differences in measuring $T_g$ of confined materials.

- In this dissertation, we have showed a wide range of possible diluent effects on slow and fast dynamics of a polymer using coarse grained approach. For specific diluents, which might be possibly be useful from industrial point of view, a atomistic simulation study can be set up to understand more about the diluent effects for a chemically realistic systems.
REFERENCES


