NANO-CONFINEMENT EFFECTS OF CRYSTALLINE WALLS ON THE GLASS TRANSITION OF A
MODEL POLYMER

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NANO-CONFINEMENT EFFECTS OF CRYSTALLINE WALLS ON THE GLASS TRANSITION OF A MODEL POLYMER

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ABSTRACT

Efforts to understand the effect of confinement on the glass transition of an unentangled polymer melt in the field of coarse-grained simulations have focused on the use of free-standing and supported films with atomistically smooth substrates. The effects these types of nano-confinement have produced are of great value when trying to understand the interfacial effects on the structure and dynamics of the material that can dominate many properties at very small length scales (< 100nm). Generally these supported and freestanding films exhibit an overall depression in the glass transition temperature $T_g$. Recently, enhanced particle dynamics have been shown near an attractive, atomistically smooth interface accompanied by a locally varied temperature dependence (fragility) of glass formation. However, an atomistically smooth force field wall omits several key physical features of nano-confinement by real solid substrates; specifically, it lacks any of the atomic structure that exists in these systems, which alters packing in glass-forming liquids near the interface and hinders motion in the transverse directions. This is particularly problematic in sheared systems where a lack of atomistic wall structure would lead to highly unrealistic boundary dynamics, for example, dynamics in a nano-fluidic device or in porous media.

The present study aims to incorporate two attractive, fixed crystalline walls in a similar study of these nano-confinement effects. Currently employed bead-spring models used in the previously discussed studies have been shown to heterogeneously crystallize when confined by crystalline walls despite exhibiting homogeneous crystallization resistance, and therefore a new model has been developed to evaluate this and other problems. The new model is a bond length modification of the Finitely Extensible Non-Linear Elastic (FENE) model, named the short-FENE. An examination of the bulk glass formation properties of multiple bond length variations of the short-FENE model shows that it can be used to tune the
breadth and abruptness of the glass transition (fragility) without requiring the use of an additive. When crystalline walls confine the short-FENE model, it exhibits an increase in $T_g$ and fragility relative to the bulk. Also the wall is shown to hinder particle motion and produce the expected increase local particle relaxation times.
DEDICATION

This thesis is dedicated to my parents. Their unconditional love and support has been invaluable in every aspect of my life, especially throughout the process of conducting the research presented here.
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CHAPTER I

INTRODUCTION

Polymer processing at the nano and micro scales has become a reality, not only in research but for real applications in many commercial products, such as microfluidic devices (e.g., inkjet printer heads), nano-layered films (e.g., filtration membranes), or flexible electronics. Processes, such as nano-lithography and nano-imprinting, also require knowledge of glass transition behavior variations upon confinement for successful product design. Answering some questions about the physics of these systems could provide valuable tools for engineering solutions in these fields. For example, what is the effect of nano-confinement on the position of the glass transition temperature? Have the materials’ properties shifted so far that the material is no longer mechanically stable in the same temperature range as the bulk, i.e., do changes in glass transition behavior seriously alter the films’ properties? This study presents new insights into nano-confinement effects of crystalline walls on a broad range of polymeric materials that can be represented by coarse-grained bead-spring models.

Before discussing changes in the properties of these materials when subjected to a confined geometry, it should be noted that despite the ubiquitous nature of the glass transition, a thorough, generally accepted theoretical understanding of its driving mechanisms has evaded scientists, engineers, and physicists\textsuperscript{1,2}. Efforts to study the transition have produced many theories, such as the Gibbs-Dimarzo\textsuperscript{3} configurational entropy theory, the Adam-Gibbs\textsuperscript{4} theory, and the mode-coupling theory\textsuperscript{5}, to name a few. This problem leads to even more difficulty when evaluating nano-scale confinement effects on the glass formation behavior of polymers, because a single standing framework cannot be applied \textit{a priori} but rather...
a range of phenomena must be evaluated, including the length scale of dynamic heterogeneity and shifts in the various characteristic temperatures predicted by different models.

Many studies conducted in this area have generally focused on nano-confinement effects in supported films with varied substrates in both simulations and experiments. Also, work has been done in free standing films. The effects these types of nano-confinement produce are of great value when trying to understand the interfacial effects on the structure and dynamics of the material that can dominate many properties at such small length scales (< 100nm). Specifically, these approaches have provided powerful insights into the behavior of elastic properties, overall shifts in the glass transition temperature, and most recently, local variations in the temperature dependence of the transition.

As the thickness of a film becomes sufficiently small, the type of interaction (attractive or repulsive) and the morphology of the confining surface become of paramount importance to the observed behavior in the properties. According to recent simulations, a smooth confining surface produces enhanced dynamics near the wall and a decrease in overall T_g, but a locally increased temperature dependence (fragility). This increase in mobility is also seen near a free surface, because the particles have more degrees of freedom due to a locally decreased density. This result is interesting, because an attractive interaction with the substrate has been shown to inhibit mobility, i.e., lower degrees of freedom, and decrease T_g. In order to reproduce this effect in a simulation, a smooth wall cannot be used, because it allows the film to move freely in the contact layer, i.e., no wall particles are present to frustrate packing, and inhibit lateral dynamics, as would be in a real system. The present study aims to evaluate this effect by using fixed crystalline walls to confine an unentangled, glass-forming, bead-spring polymer.
CHAPTER II

CONFINEMENT OF UNENTANGLED GLASS FORMING BEAD-SPRING POLYMERS BETWEEN CRYSTALLINE WALLS: A CRYSTALLIZATION RESISTANT MODEL

Introduction

As previously discussed, most every study into the effect of confinement on the glass transition has focused on the use of a force field wall or a free surface as the interface. However, an atomistically smooth force field omits several key physical features of confinement by real solid substrates; specifically, it lacks any of the atomistic structure that exists in these systems, which alters packing in glass-forming liquids near the interface and hinders motion in the transverse directions. This is particularly problematic in sheared systems, where a lack of atomistic wall structure would lead to highly unrealistic boundary dynamics, for example, dynamics in a nano-fluidic device or in porous media (e.g., in oil extraction). Furthermore, as will be described, existing coarse-grained models for polymer glass formation are unsuitable for use with crystalline walls; the focus of this particular study is, therefore, to develop a coarse-grained polymer model suitable for studying glass formation under confinement between crystalline walls.

The bead-spring polymer model, initially proposed for discussions of solution thermodynamics by Rouse and Zimm, has been extensively used in various forms both in bulk\cite{13,14,15} and confined\cite{6,7,16} geometries. In studies of glass formation, there are two forms that have been well characterized in the bulk, the harmonic\cite{13} and Finitely Extensible Non-linear Elastic (FENE)\cite{15,17} models, both exhibiting good homogeneous crystallization resistance because of an energetic length scale mismatch in the bonded and non-bonded interactions\cite{15}. Furthermore, studies of confinement effects using both models have been able to
reproduce trends seen in experiments, such as depression of the glass transition temperature\(^7,16,19,20\), using atomistically smooth force fields and free surfaces.

A few points could be raised about the applicability of these models to certain situations. First, a recent study of the harmonic model in the bulk has shown that long equilibration times can yield crystallization\(^14\); hence, the harmonic model does not strongly resist homogeneous nucleation. Second and more importantly, neither model’s crystallization resistance has yet to be fully characterized when confined by rigid crystalline walls, which can provide a potentially good nucleating surface. In an attempt to observe the effects of such a wall on the FENE model, Baschnagel et al. imposed a simplified crystalline lattice\(^21,22\). The wall structure used in this study allowed wall atoms to fluctuate around their lattice sites on weak harmonic tethers, producing a soft, albeit crystalline, wall as if a layer of hydrocarbons had adsorbed onto a hard substrate\(^21\). Crystallization was not observed in this system, a result that is not sufficiently robust because the weak harmonic tethers for the wall beads may have negated any nucleation effect that the surface would impose if stiffer springs were employed. Also, the extent of equilibration accessible at the time of this publication may not have been long enough to observe the crystalline state\(^23\). Hence, heterogeneous nucleation may be a problem for the FENE model when using fixed crystalline walls at sufficiently long equilibration times.

In order to study confinement effects on the glass transition using a more realistic interface than an atomistically smooth wall, a model that forms a glass in the bulk and under confinement between crystalline walls must be used. To rigorously evaluate the validity of the harmonic and FENE models, the energetic mismatch in bonded and non-bonded interactions must be evaluated. This frequently used argument states that frustration in packing due to a difference in the length scale associated with the minimum in the energetic potential causes homogeneous crystallization resistance, particularly in the FENE model\(^18\), insofar as the monomer beads are concerned. Crystallization could still occur if the entire chains were allowed to stretch into rods and stack at the non-bonded energetic minimum, a situation that could happen and frequently does in real polymers, but this case is not considered here as the kinetic barrier is very large. This process would be so slow that it would be difficult to reproduce on the time scale of a simulation; also much longer range motion would be necessary than can be seen in the simulations
discussed. The following evaluation of the potentials helps to clarify this situation, with a plot in Figure (1) describing the mismatch.

In the harmonic and FENE models, bead interactions are described by a single potential for each interaction type. Non-bonded interactions are calculated via the 12-6 Lennard-Jones (LJ) form in both models, given by

$$E_{LJ}(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right] + \epsilon$$  \hspace{1cm} (1)

where $\epsilon$ is an energy scaling parameter; $\sigma$ is a length scale related to the excluded volume of the beads; and $r$ is the distance between two beads. All non-bonded polymer beads interact with $\sigma = 1$ and $\epsilon = 1$ with the interaction truncated at $2.5\sigma$ and the potential shifted to zero at this cutoff. The bonded interactions describe the key distinction between the polymer models, as discussed previously. The harmonic model employs a Hookean (harmonic) spring potential

$$E_{\text{harmonic}}(r) = \frac{1}{2} K (r - r_0)^2$$  \hspace{1cm} (2)

where $K$ is a stiffness constant; and $r_0$ is the equilibrium bond length. The standard form\textsuperscript{7,14,24} of this model employs $K = 2000$ and $r_0 = 1\sigma$. In contrast, the FENE model employs for bonded interactions the potential originally introduced by Kremer and Grest\textsuperscript{25}

$$E_{\text{FENE}}(r) = -\frac{1}{2} K R_0^2 \ln \left[ 1 - \left( \frac{r}{R_0} \right)^2 \right] + 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right] + \epsilon$$  \hspace{1cm} (3)

The first term of the model is cut off at $R_0$ due to a singularity in the logarithm, providing for a maximum extensibility of the bond with stiffness described by $K$. The second term is taken from the LJ potential and is representative of the excluded volume with a cutoff at $r = 2^{1/6}\sigma$, where $\sigma$ and $\epsilon$ have analogous meanings to their use in the LJ non-bonded potential, the size of the excluded volume and the energy scale, respectively. The standard application\textsuperscript{15} of this model employs values of $K = 30$, $R_0 = 1.5\sigma$, $\sigma = 1$, and $\epsilon = 1$ and will be referred to as the standard-FENE model. A main advantage of this model is the maximum extensibility at $R_0$, which results in bond crossing resistance that has been well documented\textsuperscript{26} and is especially important in non-equilibrium molecular dynamics simulations, such as in studies of flow.
As described previously, there are potential problems with both the harmonic and FENE models, so a modified FENE potential will also be analyzed. In the spirit of the mismatch argument, this modification will be a shortening of the equilibrium bond length. The choice of parameters for this “short-FENE” model maintains desirable features, such as resistance to bond crossing and a maximum extensibility. Features such as these are expected to be retained because the functional form of the potential has not changed, only the position of the curve is adjusted; horizontal and vertical shifts are the result of changing the FENE parameters. This short-FENE model is given by a FENE form using values of $K = 30$, $R_0 = 1.3$, $\sigma = 1$, and $\epsilon = 1$. The harmonic model was not shortened, because it has been shown to crystallize homogeneously, and its mismatch with non-bonded interactions is worse than the FENE model, suggesting that it may be more prone to crystallization if this argument proves to be the driving factor in this problem, see Figure (1).

Figure 1 Plot of energetic potentials used in glass-forming bead-spring polymer simulations. The minimum 12-6 LJ potential (blue) is at $r \approx 1.12\sigma$, which differs from the harmonic (red) and FENE (green) equilibrium bond lengths at $r \approx 1\sigma$ and $r \approx 0.96\sigma$, respectively; short-FENE (black) produces an equilibrium bond length of $r \approx 0.79\sigma$ which provides for a large increase in the minimum energy required to co-exist on both potential curves.
Comparing all potentials, the minimum energy required to satisfy both the non-bonded and bonded potentials is the important feature, because matching each curve is the easiest way for a model to form a regular crystalline lattice. Of all the bonded potentials, the harmonic provides for the lowest energy scale at \( \approx 0.75 \frac{kT}{\epsilon} \), with the FENE following closely at \( \approx 1.0 \frac{kT}{\epsilon} \), and the short-FENE producing a five-fold increase at \( \approx 5.0 \frac{kT}{\epsilon} \). The greatly improved energetic barrier of the short-FENE model is expected to produce a strong crystallization resistance, and the FENE potential provides the added bonus of proven bond-crossing resistance that the harmonic model lacks (important for studies of shear flow). It may be possible to create a “short-harmonic” model, but the long term goal of this study is to evaluate shear flow, meaning bond-crossing resistance is a necessity.

Methodology

Based on the previous discussion and preliminary results demonstrating highly crystalline structures, the harmonic model is not considered. Only the FENE and short-FENE models are simulated in the present study, because their predicted resistance to heterogeneous crystallization is the highest.

Simulations

The bead-spring models studied consist of 200 linear chains of \( N = 20 \) bead length, producing an unentangled polymer melt; \( N_e = 35 \) for the FENE model\(^{26} \). Previous studies have characterized the glass formation properties of this or similar chain lengths in the bulk state for both the FENE\(^{15} \) and harmonic\(^{13,14} \) models. Energetic potentials for the interactions between beads are described in the introduction, with a 12-6 LJ potential for non-bonded (Van der Waals) interactions. Two bond models are studied: first, the standard (Kremer, Grest\(^{25,26} \) or Bennemann\(^{15} \)) implementation of the FENE model, the standard-FENE, and the short-FENE model introduced previously.

The chains were confined by walls designed with a crystalline structure bounding the polymer in the \( z \)-direction. Each wall consists of 396 identical beads fixed in lattice positions on two layers of an FCC unit cell of density \( \rho_w = 1.4 \) and the (111) face exposed to the fluid. This plane of the unit cell was chosen
as the interface, because it contains the most tightly packed configuration that corresponds to a shortest nearest neighbor distance of 1.0$\sigma$. The unit cell size determined the fixed $x$ and $y$ simulation box dimensions of $L_x = 12.0\sigma$ and $L_y = 13.9\sigma$, whereas the $z$-dimension was permitted to vary during NPT simulations. Each monomer bead interacted with the fixed wall beads via the 12-6 LJ potential described in Equation (1) with interaction parameters of $\sigma_{12} = 1.0$, $\epsilon_{12} = 0.9$ and a cut-off of $r = 2.5\sigma$. The center-to-center wall thickness of the two layers is sufficient to prevent the monomer beads from feeling the effect of the void space; effectively, the fluid experiences an infinitely thick wall with infinite mass.

All simulations of the melts were performed with the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS\textsuperscript{27}) software package using a reversible reference system propagator algorithm (RESPA) time integration scheme with a time step of $\Delta t = 0.01\tau$, where $\tau = \sqrt{\frac{1}{m\sigma^2}}$ is the LJ unit of time. Thermostatting was performed in only the $y$-dimension by using the Nos -Hoover thermostat with a damping factor of $2\tau$ in the same fashion as that done by Preizjev\textsuperscript{28}, who used a Langevin thermostat in the study of flow dynamics. This choice is motivated by the previously mentioned goal of extending the results of this study to shear flow. In these non-equilibrium studies, thermostatting with the flow direction or perpendicular to the wall would introduce an aphysical bias to the velocities of the particles under an imposed flow field; hence an anisotropic thermostat is required. Checks were performed to ensure results were not adversely effected by this choice, specifically, the temperature was closely monitored at all times by calculating its value based on each direction independently and with all three directions concurrently; time-average values obtained from all four calculations did not appreciably differ (this is also ensured because of the Equipartition Theorem). All constant pressure simulations were conducted by using the Nos -Hoover barostat restricted to resizing the box only in the $z$-direction at $P = 0$ with a damping parameter of $2\tau$. 

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Periodic boundaries are imposed in all directions, with the confining walls separated by a void space located in the center of the simulation box. This configuration was chosen to allow NPT simulations to be performed. The film should be viewed as an ultra-thin layer of polymer confined by two infinite crystalline slabs. Initial positions of the 200 polymer chains were generated in a low-density configuration using Packmol, and high temperature molecular dynamics were then conducted in the NPT ensemble for $1 \times 10^5 \tau$ at $T = 1.2$, where $T$ is the reduced LJ temperature. This procedure created a well-equilibrated starting configuration above the glass formation regime of the models. Also in the NPT ensemble, a linear quench was subsequently performed from $T = 1.2$ to $T = 0.35$ at a rate corresponding to a characteristic scale of $1 \times 10^6 \tau / T$. Following the quench, a range of temperatures was equilibrated for a length of time based on the segmental relaxation time $\tau_\alpha$ of the chains determined from preliminary data. These values were obtained by estimating the value of the self-part of the intermediate scattering function at $e^{-1}$ (not shown). Where possible, the equilibration was of length $100 \tau_\alpha$ with a minimum length of $80 \tau_\alpha$ at the coldest temperatures evaluated; this produced a maximum equilibration length of $1 \times 10^6 \tau$. The simulation

<table>
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<th>$t_{pr}$</th>
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<tr>
<td>$0.53 \geq T \geq 0.47$</td>
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<td>$10^3$</td>
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<td>$0.85 \geq T \geq 0.65$</td>
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<td>$6.6 \times 10^3$</td>
</tr>
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<td>$0.65 &gt; T \geq 0.55$</td>
<td>$10^5$</td>
<td>$6.6 \times 10^3$</td>
</tr>
<tr>
<td>$T = 0.50$</td>
<td>$10^5$</td>
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</tr>
<tr>
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<td>$10^5$</td>
<td>$9.3 \times 10^4$</td>
</tr>
<tr>
<td>$T = 0.44$</td>
<td>$10^5$</td>
<td>$1.1 \times 10^5$</td>
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<td>$10^5$</td>
<td>$2.8 \times 10^5$</td>
</tr>
<tr>
<td>$0.42 &gt; T \geq 0.40$</td>
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Table 1: Equilibration and production schedules for the nano-confined FENE model simulations. The standard-FENE model crystallized during the equilibration period leading to short production runs for static analysis of the crystal. The short-FENE model formed an amorphous film was produced by using an exponential time spacing scheme.
box was subsequently resized in the z-direction to reflect the average density over the second half of the equilibration. Production simulations were then conducted in the NVT ensemble; all simulation times are described in Table (1).

Evaluating Crystallization Resistance

A series of metrics was used to characterize the crystallization resistance of these cooled and annealed systems. The first order check for crystallization was a visual one, where the particles were viewed in both three-dimensional and projected two-dimensional space by using the Visual Molecular Dynamics\textsuperscript{30} software package. Along with this visual determination of crystallinity, a more rigorous verification was employed. The static structure factor, or Fourier transform of the particle density, was calculated in three dimensions on the whole and various subsets of the film particles, with subsets determined as described in the “Results” section. The form used to calculate these values is

\[
S(k) = \frac{1}{N} \sum_{n=1}^{N} \sum_{m=1}^{N} e^{-i k \cdot r_n} e^{i k \cdot r_m}
\]  

(4)

where \(k\) is a wavenumber corresponding to an inverse length scale; \(r_n = (x_n, y_n, z_n)\) is the position of the \(n\)th (or \(m\)th) bead; and \(N\) is the number of polymer beads included in the calculation\textsuperscript{31}. The longest length scale evaluated (as \(k \to 0\)) corresponds to the minimum box dimension: \(L = 12.0\sigma\). Equation (4) is intended for use in a system at an equilibrium state, in which the calculation would then be an ensemble average. To ensure that the quantity obtained is the true static structure factor an average over time is computed, and four statistical replications are considered for each data point. The replications and time averaging have been considered to ensure that the resulting structure factor provides an accurate representation of the nano-confined polymer film.

In evaluating the results of the structure factor, observation of sharp peaks corresponds to crystalline ordering, whereas absence of these peaks along with a very smooth curve is considered to be
amorphous. To compare the relative order of different configurations, two metrics’ temperature dependence were drawn from these plots: the height in the first peak, $H_S(T)$, and the width of that peak evaluated at half of the difference between the first maximum and first minimum, referred to as $W_S(T)$. A large, sharp first peak corresponds to ordering at multiples of the nearest neighbor distance, whereas sharp peaks at higher wavenumbers reflect other frequencies at which particles repeat in a crystalline manner. The value of $W_S(T)$ is another measure inversely related to nearest-neighbor ordering. The data computed was plotted in a discrete manner, which did not allow for the exact width of the peak to be calculated. Therefore, the width is approximated by linearly interpolating between each of the data points and using the resultant piecewise linear function.

Results

In order to analyze the relative degree of crystallization in each polymer film, the structure factor of the entire film thickness is compared for each model along with a layer-by-layer analysis of the short-FENE model.

The Standard-FENE Model

A very sharp first order peak is present in all temperatures evaluated for the standard-FENE, $0.53 \geq T \geq 0.47$. As temperature decreases, there is little increase in the height of this peak (changes are nearly within a single standard deviation) suggesting that the film has already transitioned into the crystalline phase before the highest temperature evaluated is reached, i.e. in Figure (2) $T \leq T_m$. Evaluation of $H_S(T)$ and $W_S(T)$ yields maximum values of $H_S(T = 0.47) = 7.62 \pm 2.40$ and $W_S(T = 0.47) = 0.54 \pm 0.28$. Two higher-order Bragg peaks are observed, indicative of distinct in-plane ordering. A $10^5\tau$ longer equilibration provides only a marginal increase in the height of the first peak (not shown), enforcing the conclusion that the crystalline structure is reasonable well developed.

A visual analysis of the film with a small rotation about the z-axis, i.e., a direct yz-plane projection, allows confirmation of a crystalline structure, as shown by the structure factor and is shown in
Figure (3); this and further images have been created with the rendering software Tachyon\textsuperscript{32}. A similar configuration is observed for the whole temperature range, in agreement with the degree of ordering implied by the range of temperatures shown in Figure (2).

Figure 2 Structure factor of the total standard-FENE model film. Shown at all temperatures (left) and at $T = 0.47$ (right) where a maximum value of $H_S = 7.62$ is observed at a length scale corresponding to $0.86\sigma^{-1}$ with a width $W_S = 0.54$; higher order peaks are observed at length scales of $0.61\sigma^{-1}$ and $0.50\sigma^{-1}$.

Figure 3 The equilibrated standard-FENE model at $T = 0.49$. A two dimensional projection view of the three dimensional simulated melt is shown rotated about the $z$-axis five degrees to demonstrate the imperfect, but highly crystalline, grain. Filled blue circles represent monomer beads and filled gray circles represent wall particles; bead diameters are not representative of true relative size.
The Short-FENE Model

Of all temperatures evaluated, two are chosen as specifically representative of the film’s structure. The first, \( T = 0.47 \), is used because it produces the sharpest first peak in the standard-FENE model and provides a good point for comparison. The second, \( T = 0.65 \), is chosen for comparison to results of the interfacial effect on the structure.

The short-FENE model \( S(k) \) produces values of \( H_S(T = 0.47) = 1.8 \pm 0.01 \) and \( W_S(T = 0.47) = 2.98 \pm 0.12 \). This is evidence of a relatively strong crystallization resistance when examined in comparison with the standard-FENE values. Also, the plot represents a more amorphous structure at higher order wavenumbers, i.e., smooth humps are present rather than sharp peaks. There is no temperature at which the height or width of the short-FENE model compares to the standard-FENE, as shown in Figure (5). This result demonstrates a strong resistance to the development of a crystal on the length of the entire film’s thickness. Also calculations of the structure factor were conducted before the production runs, and over the length of the production run. The results in Figure (4) and in all further analysis contained in this section are robust; they and do not change appreciably depending on the state of equilibration.

Figure 4 The structure factor of the total short-FENE film. Shown at every temperature evaluated (left) and \( T = 0.47, 0.65 \) (right), error bars corresponding to one standard deviation lie within the data point. Small peaks resembling an ordered structure that deviates from the smooth curve are identified by arrows at wavelengths of \( 0.89 \sigma^{-1} \), \( 0.57 \sigma^{-1} \), and \( 0.33 \sigma^{-1} \).

The short-FENE model \( S(k) \) produces values of \( H_S(T = 0.47) = 1.8 \pm 0.01 \) and \( W_S(T = 0.47) = 2.98 \pm 0.12 \). This is evidence of a relatively strong crystallization resistance when examined in comparison with the standard-FENE values. Also, the plot represents a more amorphous structure at higher order wavenumbers, i.e., smooth humps are present rather than sharp peaks. There is no temperature at which the height or width of the short-FENE model compares to the standard-FENE, as shown in Figure (5). This result demonstrates a strong resistance to the development of a crystal on the length of the entire film’s thickness. Also calculations of the structure factor were conducted before the production runs, and over the length of the production run. The results in Figure (4) and in all further analysis contained in this section are robust; they and do not change appreciably depending on the state of equilibration.
Despite the large difference in the height of the first peak and the relative shapes of the plots from each model suggesting the short-FENE strongly resists crystallization, there are some wavenumbers where the short-FENE model exhibits relatively small peaks when the structure factor is averaged over the entire film, a result not expected in the $S(k)$ for an amorphous fluid. The deviation from the generally smooth curve suggests that these peaks may be weak Bragg peaks. A proposed reason for these peaks is that there is weak in-plane ordering in the few layers near the wall, skewing the results in a more crystalline direction, despite a largely amorphous film. To evaluate this argument, a simple spatial decomposition scheme was implemented to isolate specific layers of the film parallel to the wall. An interfacial region contains all particles within $3\sigma$ of the center of the first layer of wall beads, and the central region contains all particles a minimum of $6\sigma$ from the same point on each wall. This scheme created five regions of the film: two interfacial regions of thickness $3\sigma$, two buffer zones of thickness $3\sigma$, and one central region whose thickness varied with temperature; this is schematically described in Figure (6). This decomposition scheme has been employed previously in the study of interfacial induced ordering in the first fluid layer of the standard-FENE model, with the distance of 5-6\sigma corresponding to the length scale where a uniform density profile is obtained\textsuperscript{33}; the same check has been performed in Figure (6). The $S(k)$ for each domain was calculated, and then, an average was performed over all bins of the same type and temperature; results are shown in Figure (6). Analysis of spatial regions in the film yields a curve that describes a truly
amorphous structure in the central region with sharper, more crystalline peaks seen in the interfacial region corresponding to the same wavenumbers as those in the total film structure factor.

![Graph and schematic](image)

Figure 6  An example density plot of half the channel (left) at $T = 0.65$, and a schematic of the spatial decomposition for structure analysis (right). In both images $z = 0$ is the center of the first layer of wall particles, and red lines are bin boundaries. The two halves of the film are considered independent, and the density profile is an average over the length of the production run. The second layer exhibits two peaks: the first representing beads bonded to the wall adjacent layer, and the second to the non-bonded nearest neighbors of the wall. In the schematic the regions are not drawn to scale and buffer zones are marked with hash marks.

In the interfacial region, see Figure (7), sharp peaks occur at multiple length scales, the same wavelengths as identified in Figure (4). These features are seen at all temperatures studied (not shown), although they are most prominent in the range $0.65 \geq T \geq 0.60$. This temperature range is expected to represents the best combination of kinetic and thermodynamic driving forces for heterogeneous crystallization that this wall can provide, and it can be seen by comparing these results with the central region that this in-plane ordering has decayed completely once the film center is reached. The length scale to which the ordering persists corresponds closely to the number of distinguishable layers displayed by the density, i.e., the central region has a constant density and also lacks any defined structure when compared to the layered interface. Whether the observed structure is due purely to fluid layering was investigated by further decomposing the interfacial region in an effort to isolate any in-plane ordering.
The decomposition is done with a relatively crystalline temperature $T = 0.60$ by dividing the interfacial region into three bins. Here, bins correspond to layers of a thickness $1\sigma$ beginning at an offset of $0.5\sigma$ from the center of the wall beads, i.e., each bin is the size of one layer of particles based on their non-bonded radius of $\sigma$. The calculation of the structure factor for these regions is done in a “symmetric” manner, that is, in Equation (4) both summations are taken over only the particles contained in the bin. Thus any structure presented by the results can only correspond to the particles in that specific layer (results represent in-plane ordering, not layering). Figure (8) shows the wall adjacent fluid layer as very structured and the data appears noisy due to a relatively high degree of in-plane ordering. The first peak for this layer is at the same length scale as the other plots $0.89\sigma^{-1}$ with a height of $3.33 \pm 1.35$. This result is still
significantly lower than the maximum standard-FENE peak of 7.15. The second and third layers have small (< 1.5) peaks at this length scale along with relatively small higher order peaks. This demonstrates that particle ordering is all but eliminated within a short distance from the wall (≤ 3σ), as the energetic cost of the ordering beyond the first two layers is too high. As described in the introduction, see Figure (1), the model cannot produce a configuration on a length scale compatible with both the bonded and non-bonded potentials that allows monomers to assume a local crystalline structure, and thus nucleate a long range crystalline lattice.

An example image of this model is shown in Figure (9) alongside the standard-FENE; both are at the same temperature, T = 0.49, and 2D rotational projection of the 3D system is as that in Figure (2). The change in the equilibrium bond length introduced in the short-FENE model created a higher density film due to bonded neighbors having less excluded volume; hence, the film is thinner. The extent of the structure in the interfacial region is confirmed, because a third layer is difficult to resolve visually.

Figure 8 Interfacially decomposed structure factor of the short-FENE model at T = 0.65. The wall adjacent (left) and next two layers (right) are all one σ thick. Arrows denote wavenumbers presented in previous figures. Error bars refer to an average over eight replications of the layer, one for each interface simulated.
Conclusions

The standard-FENE model readily undergoes heterogeneous crystallization when confined between walls that provide a favorable template, i.e., a fixed crystalline lattice that has a packing length scale near to that of the bonded and non-bonded interaction energetic minimum. The length scales corresponding to the standard-FENE model’s interaction potentials only differ by \( \approx 0.16\sigma \) producing a scaled energetic difference of \( \approx 1\ kT/\epsilon \) that does not provide an adequate thermodynamic barrier to crystallization. Therefore, this model cannot be used to study confinement effects on the glass transition where crystalline walls are employed. As described in the introduction, incompatible length scales can be created by shortening the bond and therefore creating a larger energy mismatch. The short-FENE model
has this larger length scale mismatch at \( \approx 0.33\sigma \) and subsequent five-fold increase in the energetic mismatch; hence, it solves the problem of a thermodynamically stable crystalline state. As described by the difference in the several structure factor calculations for the short-FENE model, the film is amorphous throughout nearly the entire film thickness; only a small amount of in-plane ordering is present in the wall adjacent fluid layer.

Prior to evaluating the nano-confinement effect of the crystalline walls on the film described herein, the short-FENE model’s glass transition behavior must be fully evaluated in the bulk. Chapter III contains this bulk characterization for the model discussed previously, along with two other bond lengths in order to determine other trends in behavior beside only crystallization resistance. Confinement effects on the glass transition of the short-FENE model will then be examined at length in Chapter IV.
INTRODUCTION

An opportunity provided by modifying the FENE potential is the possibility of tuning the characteristic properties of the melt, such as the position of characteristic temperatures or the fragility, i.e., strength of glass formation. Many studies have been done to show the effect of additives on the glass transition\(^7,14,17,24\), which provides an effective way to tune glass formation behavior. If this same effect could be produced by simply varying the FENE bond length, this would be very useful for studies in a variety of polymeric systems, such as nano-layered films with identical topology but varied fragility or glass transition temperature, \(T_g\). Rapid simulations could be conducted by re-using the same model with only a small change of parameters; this small change could easily produce qualitatively different results and therefore easily determine the effect of varying bulk fragility and \(T_g\) on varied confinement geometries.

METHODOLOGY

In this study, four FENE model bead-spring melts are investigated in their bulk configuration to determine changes to glass formation behavior based on a varied equilibrium bond length.
Simulations

The melts consist of 100 bead-spring chains of length $N=20$, chosen to be below the entanglement length for a standard-FENE model (a standard-FENE bond and three modified short-FENE models, which are produced by a change of parameters given in Table 2). All simulations were conducted by using the LAMMPS software package. Thermo and barostatting were again performed by using the Nosé-Hoover algorithm, but all three box dimensions varied in a coupled manner to adjust pressure, unlike the confined study of Chapter II. Also, thermostatting was conducted in all directions, because bulk studies do not necessitate a one-dimensional thermostat.

<table>
<thead>
<tr>
<th>Equilibrium bond length, $l_{eq}$</th>
<th>$K$</th>
<th>$R_0$</th>
<th>$\sigma$</th>
<th>$\epsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.96</td>
<td>30</td>
<td>1.5</td>
<td>1.0</td>
<td>1</td>
</tr>
<tr>
<td>0.90</td>
<td>30</td>
<td>1.4</td>
<td>0.9</td>
<td>1</td>
</tr>
<tr>
<td>0.79</td>
<td>30</td>
<td>1.3</td>
<td>0.8</td>
<td>1</td>
</tr>
<tr>
<td>0.70</td>
<td>30</td>
<td>1.2</td>
<td>0.7</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 2 Parameterization of the bonded potential for all bulk FENE models studied. The standard model is given by a length of $0.96\sigma$, with the short-FENE model described in the previous chapter given by a length of $0.79\sigma$.

Table 3 Equilibration and production schedules for bulk FENE model simulations.

<table>
<thead>
<tr>
<th>$l_{eq}$</th>
<th>$t_{eq}(\tau)$</th>
<th>$t_{pr}(\tau)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.96 $\geq l_{eq} \geq 0.79$</td>
<td>$10^3$</td>
<td>$102\times10^3$</td>
</tr>
<tr>
<td>$1.00 \geq T \geq 0.56$</td>
<td>$10^3$</td>
<td>$7.58\times10^3$</td>
</tr>
<tr>
<td>$0.55 \geq T \geq 0.51$</td>
<td>$10^4$</td>
<td>$1.17\times10^5$</td>
</tr>
<tr>
<td>$0.50 \geq T \geq 0.46$</td>
<td>$10^5$</td>
<td>$1.00\times10^6$</td>
</tr>
<tr>
<td>$T \leq 0.45$</td>
<td>$10^6$</td>
<td>$1.00\times10^6$</td>
</tr>
</tbody>
</table>

Periodic boundary conditions were imposed in all directions, and the procedure and software used to prepare the melts is identical to the confined study. The cooling rate, ensemble variation, and box resize

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procedure also are retained. One significant differentiating factor in the bulk studies is the equilibration and production schedule, outlined in Table (3). Equilibration lengths are chosen to be a minimum of 80$\tau_a$ as described in the previous chapter.

**Evaluation Techniques for Glass Formation**

The melts are characterized by a few methods in addition to the structure factor analysis described in Chapter II. The Debye-Waller factor (DWF), $\langle u^2 \rangle$, representing the rattle volume of particles or the timescale a particle is stuck in a transient cage of its nearest neighbors$^{34}$, as a function of temperature is calculated by taking the value of the mean-squared displacement of monomer particles where $t = 0.95\tau$ for all temperatures. This is the closest time to $\tau$ recorded in this study, which has been shown to produce quality results for evaluating the DWF in simulations of the bulk harmonic model$^{14}$.

To determine the characteristic temperatures of the glass transition, relaxation processes must be evaluated, and the segmental relaxation time of the monomer particles $\tau_a$ is used for this purpose. It is determined by first calculating the self-part of the intermediate scattering function, which describes the rate at which a particles’ position decorrelates from a past position. The definition employed at the first peak in the structure factor $k^*$ has the form

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

where $k$ is the peak wavevector; $t$ is the time; $r_j(t)$ is the position vector of the particle; $N$ is the number of particles; and brackets denote an ensemble average$^{31}$. The relaxation time is then calculated by using a stretched exponential (Kohlrausch–Williams–Watts) fit of the form

$$F_S(k^*, t) = A \exp \left( - \left( \frac{t}{\tau_a} \right)^\beta \right)$$

where the pre-factor, $A \in [0,1]$, is a fitting parameter; and $\beta \in [0,1]$ is a stretching exponent$^1$ describing deviation from a simple exponential decay. Not all times are used in this fit; short-time inertial motion is truncated by only using $t > 0.95\tau$. 

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The resulting curve $\tau_\alpha(T)$ produced from Equation (6) is fitted to three different forms. The first of which is used explicitly at high temperatures and is known as the Arrhenius relationship

$$\tau_\alpha(T) = \tau_A \exp\left(\frac{-E_A}{kT}\right) \quad (7)$$

where $\tau_A$ is the high temperature relaxation time, which has been observed both in simulation$^{24}$ and experimentally$^{35}$ near $10^{-13}$s. The activation energy of this relaxation process is given by $E_A$. This form is used to determine the temperature at which the relaxation time first deviates from Arrhenius dependence, algorithmically calculated by fitting the curve to all data points below $T_g$ and then iteratively removing points until a fitting goodness criterion of $r^2 \geq 0.99$ is obtained. The final point removed is considered the onset of the glass transition $T_A$.

Another fitting form describes this deviation of relaxation from the Arrhenius law and is referred to as the Vogel-Fulcher-Tammann (VFT) equation

$$\tau_\alpha(T) = \tau_0 \exp\left(\frac{DT_0}{T - T_0}\right) \quad (8)$$

where $\tau_0$ is the limit of the relaxation time at high $T$; $T_0$ is the temperature corresponding to structural arrest, i.e., a divergent $\tau_\alpha$ and $D$ is inversely related to the fragility of glass formation (higher values indicate a more Arrhenius behavior). The convention of $\tau_\alpha = 100$ s is used to define the glass transition temperature $T_g$ based on an extrapolation of the VFT curve$^1$ and the slope of this curve at $T_g$ given by

$$m = \frac{\partial \ln \tau_\alpha}{\partial \frac{T - T_g}{T}} \bigg|_{T=T_g} \quad (9)$$

is another value frequently used to characterize the fragility of glass formation$^6$, with a higher value representing more fragile behavior (known as the dynamic fragility index).

The empirical mode-coupling temperature $T_C$ is frequently used to divide the glass formation range into a high and low temperature regime$^{24}$ and is predicted by fitting the form
where $A$ is a fitting parameter; and $\gamma$ is a stretching constant representative of the breadth of the glass transition. This characteristic temperature can be viewed from a phenomenological standpoint as a divergence in slow-beta and alpha relaxation times.

A final method of characterizing the melts is the relative degree of dynamic heterogeneity as temperature decreases. This is accomplished by evaluating the temperature dependence of the peak time and value of the non-Gaussian parameter (NGP), i.e., variations of particle displacements from a fitted Gaussian curve. A large value in the NGP indicates that the related time scale corresponds to some activated dynamics at that temperature, i.e., increased string-like motion of particles. This motion is also referred to as cooperative rearrangement, leading to the definition of cooperatively rearranging regions (CRRs), the size of which have been tied to the glass transition by the Adam-Gibbs relation. This theory of glass formation classifies a temperature-dependent size of the configurational rearrangements described by the CRRs.

Results

The Debye-Waller factor of the models increases monotonically as the bond length decreases. The DWF has been shown to be inversely related to local elastic modulus; therefore, a higher value in the results, Figure (10), corresponds to a qualitatively larger local elastic modulus. This could explain the relatively large increase in the inverse DWF at the lowest bond length, because stiffness in the chain backbone would be expected to increase the modulus. This stiffness is due to a short bond, causing an increase in the preference of rod-like chain alignment, i.e., the chain effectively feels an angular dependence from the next nearest neighbors on the chain, because the length scale corresponding to non-bonded interactions is constant in all models. Finally, the relative temperature dependence of the DWF (slope of the above plot) is relatively similar in all models, with the caveat of a small shift in the standard-FENE model around $T = 0.70$ (note that this is just before the onset of the glass transition discussed at the end of this section).
The structure factor of the models, shown in Figure (11), is calculated in order to determine what length scale (wavenumber) to use when applying the self-part of the intermediate scattering function, Equation (5), and for normalization of the DWF. Another use is attempting to identify any structural trends. The first peak becomes more diffuse and less sharp with decreasing bond length, until the shortest bond is reached and the height increases again. All models display three defined peaks, but each model produces them at different length scales, consistent with the variation of the bonded potential’s minimum. As the bonded to non-bonded mismatch is increased, the melt should be expected to become less ordered according to the energetic length scale argument presented in the previous chapter.

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Shortening the bond produces an upward shift in the width of the first peak in the structure factor relative to the standard model. The values of $W_S$ presented in Figure (12) show that the $l_{eq} = 0.79\sigma$ model has the least-defined nearest neighbor peak of all bond lengths. Unlike the DWF, the temperature dependence of $l_{eq} = 0.70\sigma$ is weaker than the other bond lengths.
Figure 11 Structure factor at (a) $T = 0.85$, (b) $T = 0.55$, and (c) $T = 0.45$ for all four bulk FENE bond lengths. Error bars corresponding to a single standard deviation lie within the data point.
Figure 12 Width of structure factor of all four bulk FENE bond lengths at half the difference of the first peak $H_\delta(T)$ and the first minimum value based on interpolation between discrete points.

Figure 13 Segmental relaxation $\tau_\alpha$ vs. temperature for all four bulk FENE bond lengths. Times calculated from an average over four stretched exponential fits given by Equation (6) to the self-part of the intermediate scattering function. Dashed lines correspond to VFT fits of all temperatures reported with fitting parameters detailed in Table (4).
As described by Equations (6-7), the segmental relaxation time $\tau_\alpha$ was calculated for each melt; results are shown in Figure (13). When comparing the standard-FENE ($l_{eq} = 0.96\sigma$) to the next shortest bond length ($l_{eq} = 0.90\sigma$), a small change in relaxation times is seen at all temperatures. The short-FENE model ($l_{eq} = 0.79\sigma$) exhibits an increased $\tau_\alpha$ at all but the lowest temperatures, and the shortest bond length has longer relaxation times across the entire temperature range. In order to understand how the models’ properties change with bond length, VFT and MCT fits are initially done by using every temperature with a relaxation time less than $10^4$ producing parameters given in Table (4).

Table 4  VFT and empirical MCT fitting parameters from bulk FENE model relaxation times. Also fitting parameters from the extrapolated $T_g$ and $m$ VFT approximations. Temperatures generating a relaxation time greater than $10^4$ are not included in the fit. Error is based on a 95% confidence interval, and all fits produced a goodness of fit parameter of $r^2 \geq 0.997$.

<table>
<thead>
<tr>
<th>$l_{eq}$</th>
<th>$T_0$</th>
<th>$T_g$</th>
<th>$T_C$</th>
<th>$D$</th>
<th>$\tau_0$</th>
<th>$\gamma$</th>
<th>$m$</th>
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</thead>
<tbody>
<tr>
<td>0.96</td>
<td>0.346 ± 0.004</td>
<td>0.372</td>
<td>0.409 ± 0.001</td>
<td>2.59 ± 0.16</td>
<td>0.09</td>
<td>3.24 ± 0.081</td>
<td>216</td>
</tr>
<tr>
<td>0.90</td>
<td>0.324 ± 0.004</td>
<td>0.353</td>
<td>0.395 ± 0.001</td>
<td>3.10 ± 0.17</td>
<td>0.09</td>
<td>3.46 ± 0.098</td>
<td>183</td>
</tr>
<tr>
<td>0.79</td>
<td>0.301 ± 0.005</td>
<td>0.339</td>
<td>0.394 ± 0.001</td>
<td>4.34 ± 0.24</td>
<td>0.08</td>
<td>3.50 ± 0.076</td>
<td>136</td>
</tr>
<tr>
<td>0.70</td>
<td>0.319 ± 0.012</td>
<td>0.364</td>
<td>0.405 ± 0.012</td>
<td>4.89 ± 0.45</td>
<td>0.08</td>
<td>4.71 ± 0.595</td>
<td>122</td>
</tr>
</tbody>
</table>

Other temperature ranges were used to fit the data (not shown), such as truncating lower temperature data points and/or all temperatures above the approximation for $T_A$ given below, and the qualitative trends in the data do not change, demonstrating that the resulting conclusions are robust. As with the structure factor, some of these trends are inverted once the shortest bond length is reached; hence, further discussion will refer to the usefulness of the trends seen in the other bond lengths.

All characteristic temperatures ($T_0$, $T_g$, and $T_C$) decrease with respect to a shorter bond length, representing a downward shift in the lower temperature regime of glass formation ($T \leq T_C$) but not strictly a shift of the entire range of glass formation. The decrease in fragility demonstrated by the increase in the parameter $D$ (also decrease in $m$) and the monotonic increase in $\gamma$ show that decreasing the bond length makes the model a stronger, broader, more Arrhenius glass former (interestingly these are the only trends in parameters maintained by the shortest bond length, $l_{eq} = 0.70\sigma$). Therefore, it has been determined that the short-FENE model and its variants can be used to tune the breadth and abruptness of the bulk glass formation properties (namely, the fragility) of a polymer melt without requiring the use of an additive.
To further evaluate the characteristic temperatures, a method must be chosen to determine the onset temperature of the glass transition $T_A$. As described in the methodology, one way to do this is to find the point where the relaxation data first deviates from Arrhenius behavior; an algorithm was devised to do this with results outlined in Table (5). A general upward trend exists in $T_A$ as the bond length is decreased, consistent with the range of glass formation becoming relatively broader as the bond length becomes shorter as implied by the fragility and low temperature findings from the VFT and MCT fits. It should be noted that odd behavior in the high temperature relaxation time and activation energy in the standard-FENE model and large error in the value of $T_A$ for one of the models suggest that this method may not be well suited to even a small amount of noise in the data, because the criterion used as a cutoff is a goodness-of-fit parameter. Other methods, such as finding the first minimum in the slope of the mean-squared displacement (derivative smaller than that of the diffusive regime, i.e., the first plateau), could be employed to more accurately describe the range of this onset temperature.

Table 5 Parameters of Arrhenius fits for high temperature relaxation times of bulk FENE models. Also, $T_A$ corresponding to the highest temperature included in the fit. The temperature cutoff was chosen by removing low temperatures sequentially until the criterion $r^2 \geq 0.99$ was satisfied.

<table>
<thead>
<tr>
<th>$t_{eq}$</th>
<th>$T_A$</th>
<th>$\tau_A$</th>
<th>$E_A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.96</td>
<td>0.60 ± 0.10</td>
<td>0.638</td>
<td>0.34</td>
</tr>
<tr>
<td>0.90</td>
<td>0.70 ± 0.01</td>
<td>0.037</td>
<td>2.46</td>
</tr>
<tr>
<td>0.79</td>
<td>0.60 ± 0.20</td>
<td>0.026</td>
<td>2.94</td>
</tr>
<tr>
<td>0.70</td>
<td>0.81 ± 0.01</td>
<td>0.031</td>
<td>3.26</td>
</tr>
</tbody>
</table>

A final metric by which the models are characterized is the non-Gaussian parameter (NGP), which describes deviations of particle displacements from a Gaussian curve. A representative plot of this parameter as a function of time for all bond lengths at $T = 0.48$ is given in Figure (14). As with the first peak in the structure factor and the characteristic temperatures, there is, initially, a decrease in the peak value of the NGP with decreasing bond length, followed by an abrupt increase at the final, shortest bond length. Another measure using this parameter is comparison of the peak time value $t_{peak}$ to the structural relaxation time $\tau_\alpha$. The Stokes-Einstein relationship for a simple liquid predicts an inverse relationship between the diffusion of particles and the relaxation time $^3$, and this relation implies a proportional relationship between $t_{peak}$ and $\tau_\alpha$ since the structural relaxation time is proportional to viscosity and $t_{peak}$ is a diffusional decorrelation time scale. This relationship can break down because of dynamic heterogeneity$^{35}$,
producing a value of \( b < 1 \) in the power law relationship \( t_{\text{peak}} \sim \tau^b \). Evaluating this relationship in Figure (15), shown at the end of the chapter, an increasing value of \( b \) with increased bond length is observed, consistent with more fragile glass formation and decreased dynamic heterogeneity. The dependence of the extent of string-like cooperative motions which have previously been reported in simulation\(^{37,38}\) and predicted by theory\(^4\) will be evaluated in a future study.

![Figure 14](image-url)

**Figure 14** The non-Gaussian parameter for the each bulk polymer at \( T = 0.48 \) (left) and the time corresponding to this peak as a function of temperature (right). Higher temperature points fall along the same approximate curve (not shown). Error bars correspond to one standard deviation.

**Conclusions**

By introducing a shortened bond length to the widely used glass formation model, the FENE model, a new tool for modification of fragility (specifically reductions of fragility) in studies of glass formation, has been presented, the short-FENE model. The range to which the bond can be shortened and still maintain a monotonic change in fragility (and other characteristics, such as the height of the first peak in the structure factor and the value of the NGP) extends to a point at or above \( l_{\text{eq}} = 0.70 \sigma \). The glass transition temperature \( T_g \) and empirical mode coupling temperature \( T_C \) both exhibit a small upward shift upon adjustment of the bond length, whereas the apparent onset temperature of the glass transition exhibits a relatively larger increase (consistent with the fragility finding, i.e., a broader transition).
Now that bulk properties of the short-FENE model are known, the effect of nano-confinement between fixed crystalline walls on the glass transition can be evaluated. A bond length of $0.90\sigma$ is not guaranteed to prevent crystallization and a length of $0.70\sigma$ is too short for a simplistic study without further evaluation of any possible stiffness effects. The bond length of $0.79\sigma$ is well suited to the task, because it is proven to resist crystallization and does not appear to exhibit a large stiffness effect.

![Figure 15](image.png)

Figure 15  Relaxation times of the four bulk FENE polymers at all temperatures plotted as a function of the corresponding peak NGP time. A slope of one is represented by the dashed line (Stokes-Einstein relationship for simple liquids).
CHAPTER IV

NANO-CONFINEMENT EFFECTS ON THE GLASS TRANSITION USING CRystalline WALLS

Introduction

Now that the short-FENE model’s glass transition has been evaluated in the bulk (Chapter III) and described as a strongly resistant model to crystallization when a fixed crystalline wall is imposed as a confining surface (Chapter II) the effect that nano-confinement between two fixed crystalline walls has on the glass transition can be evaluated. This is a problem that has not been adequately studied, because there have been few reports on such systems (those with an attractive, crystalline wall) from the perspective of glass formation. As discussed in the introduction, a large number of studies\(^9\) have been conducted on static supported films using atomistically smooth confining walls, with static free-standing films, or with non-equilibrium shear flow\(^{28,33,39}\). Evaluating the change in dynamics at the nano-scale provided by an attractive crystalline wall could have many uses in porous media, micro-fluidic devices, or filtration media as previously discussed.

Methodology

The model used for this study is fully described in Chapter II, but the important points are recaptured here. A film consisting of 200 bead-spring chains of a subentanglement length of \(N = 20\) is the subject of this study. The chains interact with both non-bonded interactions given by the 12-6 LJ potential and bonds modeled by the short-FENE model with \(l_{eq} = 0.79\sigma\). The confining surfaces in the vertical direction are fixed crystalline walls that attractively interact with the fluid via a 12-6 LJ potential. The film
was generated by quenching an initial configuration in the NPT ensemble at a constant cooling rate and then subsequent equilibrations also in the NPT ensemble. Finally, NVT production runs were conducted for measurements; all simulation times are described in Table (1).

Analysis of the nano-confinement effects is restricted to the segmental relaxation time $\tau_\alpha$ of the film in comparison to the bulk results presented in the previous chapter. The fitting forms from the bulk study are employed again to the total film and with a spatial decomposition scheme similar to the one used in Chapter II to resolve dynamics as a function of distance from the wall. In this case, 28 total bins are chosen to be a fixed $\delta_z = 0.75\sigma$ thick based on the width of the first and second peaks in the density profile. Figure (16) shows that the choice of bin thickness provides that no bin will have too few particles to ensure a statistical average when the relaxation time is calculated over the length of the production run. Each side of the film is again considered to be an independent interface, giving eight data points.

![Figure 16](image)

Figure 16  Number density as a function of distance from the center of the first layer of fixed wall beads. Both halves of the film are averaged together. Vertical red lines correspond to bin boundaries for the first two bins; others are not shown.

Results

The analysis of the glass formation of the nano-confined short-FENE model is conducted by first calculating the self-part of the intermediate scattering function at the peak of the central structure factor presented in Figure (7). This value is used because it truly represents the inter-particle nearest neighbor distance of the film unlike the total structure factor, which is skewed by the small amount of in-plane ordering near the wall. Again, fitting the stretched exponential form produces the results in Figure (17) that visually indicate an upward change in both the fragility and the apparent divergence of relaxation time.
while also exhibiting a convergence to the same relaxation time at high temperature. This is quantitatively confirmed by conducting fits to the data according to the same maximum relaxation time cutoff of $10^4\tau$ used in Chapter III and comparing all fitting parameters with their bulk values. The trends seen are not affected by the range or density of temperatures used in the bulk short-FENE curve fits (not shown), so the lack of a comparable number of data points is not an issue.

As all ratios in Table (6) show, confinement between two fixed crystalline walls causes an increase in the “low temperature” glass transition regime, i.e., those temperatures below or equal to the empirical mode coupling divergence temperature ($T_0$, $T_g$, and $T_C$ all shift upward). The position of this temperature $T_C$ is also the least affected of the three presented here, which makes sense because the film is also less fragile than the bulk melt, suggesting the sub-$T_C$ dependence of the relaxation time on temperature is more severe. This increase in the low temperature relaxation times should be due to increased resistance
to particle motion near the wall, because the fixed crystalline lattice provides an inhibition to particle motion that impacts the properties of the melt at a temperature higher than where the bulk transition would occur, i.e., there is a “heterogeneous” effect on relaxation that occurs before any significant “homogeneous” decrease in the particle dynamics.

In order to examine the effect of the wall on these processes, multiple bins were created from each half of the film as described previously, and a profile of relaxation times was obtained, as shown in Figure (18). These results display an increase in the relaxation time near the wall compared to the center of the film, providing a reason for the increased overall extrapolated structural arrest temperature $T_0$. Also, the length scale to which the wall affects the relaxation dynamics is increasing to a length of greater than one-third the thickness of the film (the lowest temperature simulated produces a thickness of $\approx 18.7 \sigma$). At $T = 0.45$, there is a near to two order of magnitude increase in the relaxation time near the wall in relation to the bulk and film center values. This results in the two bins nearest the wall being out of equilibrium according to the $100\tau_\alpha$ equilibration time argument used for this study. In order to get a local picture of the dynamics, VFT fits were performed on the layer-resolved relaxation times; parameters are reported in Table (7) with a few representative results plots in Figure (19). A new, lower, cutoff of $2\times10^3\tau$ is used here as a maximum relaxation time because of slower dynamics in the interfacial region. The lower temperatures (specifically

Figure 18 Relaxation times calculated for independent (non-overlapping) bins at various temperatures (left) with error bars frequently within the data point. Also, the same data normalized by the corresponding bulk value (no error bars).
0.45 ≤ T ≤ 0.50) were not equilibrated sufficiently to allow for the 10^4τ cutoff to be used near the wall (this choice provides for a minimum equilibration period of 50τ_α for each individual layer).

Table 7  VFT fitting parameters of short-FENE segmental relaxation times as a function of distance from a crystalline wall. Only 12 fixed size bins that do not overlap at any temperature are evaluated. Data points used in the fit are average results from the eight interfaces simulated, and a maximum relaxation time of 2×10^3τ is set.

<table>
<thead>
<tr>
<th>Position z</th>
<th>T_0</th>
<th>D</th>
<th>τ_0</th>
<th>T_g</th>
<th>m</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.13</td>
<td>0.345 ± 0.114</td>
<td>5.14 ± 5.72</td>
<td>0.04</td>
<td>0.395</td>
<td>122</td>
</tr>
<tr>
<td>1.88</td>
<td>0.307 ± 0.058</td>
<td>6.10 ± 3.77</td>
<td>0.02</td>
<td>0.359</td>
<td>108</td>
</tr>
<tr>
<td>2.63</td>
<td>0.337 ± 0.024</td>
<td>3.73 ± 1.10</td>
<td>0.06</td>
<td>0.373</td>
<td>158</td>
</tr>
<tr>
<td>3.38</td>
<td>0.335 ± 0.012</td>
<td>3.45 ± 0.52</td>
<td>0.08</td>
<td>0.368</td>
<td>167</td>
</tr>
<tr>
<td>4.13</td>
<td>0.339 ± 0.012</td>
<td>3.11 ± 0.50</td>
<td>0.09</td>
<td>0.369</td>
<td>183</td>
</tr>
<tr>
<td>4.88</td>
<td>0.340 ± 0.016</td>
<td>2.91 ± 0.62</td>
<td>0.11</td>
<td>0.369</td>
<td>192</td>
</tr>
<tr>
<td>5.63</td>
<td>0.340 ± 0.012</td>
<td>2.81 ± 0.44</td>
<td>0.12</td>
<td>0.368</td>
<td>197</td>
</tr>
<tr>
<td>6.38</td>
<td>0.337 ± 0.014</td>
<td>2.92 ± 0.52</td>
<td>0.11</td>
<td>0.365</td>
<td>192</td>
</tr>
<tr>
<td>7.13</td>
<td>0.341 ± 0.018</td>
<td>2.68 ± 0.62</td>
<td>0.13</td>
<td>0.368</td>
<td>205</td>
</tr>
<tr>
<td>7.88</td>
<td>0.347 ± 0.013</td>
<td>2.41 ± 0.44</td>
<td>0.16</td>
<td>0.372</td>
<td>224</td>
</tr>
<tr>
<td>8.63</td>
<td>0.344 ± 0.016</td>
<td>2.51 ± 0.55</td>
<td>0.15</td>
<td>0.369</td>
<td>217</td>
</tr>
<tr>
<td>9.38</td>
<td>0.345 ± 0.020</td>
<td>2.47 ± 0.64</td>
<td>0.15</td>
<td>0.370</td>
<td>220</td>
</tr>
</tbody>
</table>

Examining the local impact of the wall on the fragility and glass transition temperature in the first layer of the film is difficult to do with this set of results because of a large error; D has a specifically large error. This effect is also seen in the second layer and comes from the fact that the maximum relaxation time cutoff of 2×10^3τ was applied on a layer by layer basis, i.e., the fits conducted on the wall adjacent layer and its neighbor contain even fewer data points than the other ten layers analyzed due to the increased relaxation time. Visually the first layer fit does not even cross the final two data points in Figure (19), even though they are included in the VFT fit performed.

Despite this unfortunate finding, the other layers of the film can be analyzed by comparing to the bulk values, as shown in Figure (20) at the end of the chapter. These preliminary results generally agree with the increase in fragility and structural arrest temperature T_0 found when analyzing the film as a whole. Although, it appears that the fragility is returning to its bulk value near the wall (see layers three and four, ignoring one and two). Any further conclusions require further study, i.e., calculation of the relaxation time at more temperatures and possibly longer equilibrations to allow for longer relaxation times to be evaluated as equilibrium particle dynamics. Another advantage of more data points would be the possibility to estimate the position of the onset temperature T_A of the glass transition.
Nano-confinement of the glass forming short-FENE polymer melt between fixed crystalline walls produces an increase in all characteristic temperatures of the glass transition and an increase in the fragility, or abruptness, of the transition. Layer-resolved dynamics are attempted and reveal that relaxation times near the wall increase up to 100 times the related bulk relaxation at some temperatures. This has led to only speculative conclusions about the local results, because many layers are inadequately equilibrated. Further study is necessary to completely determine the local dynamics, but a few conclusions can be suggested.

The decrease in dynamics near the wall extends up to a third of the way through the film thickness at low temperature (albeit above $T_g$). These preliminary results suggest a long range (longer than the current film thickness of $\approx 18\sigma$) effect of the fixed crystalline wall on film properties. Also, if the low quality fitting parameters in Figure (20) are to be believed, fragility is found to increase in the films center relative to bulk, whereas apparently showing a decrease near the wall. Much work needs to be done to fully elucidate the true impact of the crystalline wall on the local fragility and $T_g$ behavior of the melt. This work will be outlined along with a summary in the next chapter.
Figure 20 VFT fitting parameters as a function of distance from the wall. Error bars correspond to a 95% confidence interval. Large error near the wall for $D$ suggests more temperature points should be used in the fit; the current maximum $\tau_\alpha$ including $2\times10^3\tau$ and a low temperature density are the cause of so few data points.
CHAPTER V

CONCLUSIONS AND FUTURE DIRECTION

As described in the introduction and Chapter II, current simulation studies of nano-confined coarse-grained glass forming polymer models do not accurately capture the dynamics of particles near the confining surface(s). These studies are particularly inadequate because they lack a structured wall that provides inhibitions to lateral motion. When implementing two fixed crystalline walls in a channel configuration in an effort to elucidate the real dynamics prominently used bead-spring glass formers, the standard-FENE model and the harmonic model crystallize, even though the former has been classified\textsuperscript{18} as homogeneously crystallization resistant.

By shortening the bond length of the FENE model, this crystallization problem is avoided by increasing the energy level necessary for bonded and non-bonded interactions, and therefore, removing any acceptable crystalline state when the fixed confining walls are imposed. Bulk studies of these modified FENE models exhibit the added benefit of an ability to tune the glass formation properties, such as increasing $T_g$ and decreasing fragility by shortening the bond length below the standard-FENE length. It has also been found that shortening the bond too far reverses the trend in $T_g$ due to a possible stiffness effect in the polymer backbone; the cause of this effect is to be further evaluated. There are many applications where tuning the fragility and position of $T_g$ by changing the bond length would be very useful, for instance, in nano-layered films specifically because this method does not require the use of an additive which may prefer one layer more than the other. Also, this model does not require modifications of
topology, such as addition of side-groups, only a small backbone modification is necessary to tune the glass transition properties.

Using one variant of this new model, named the short-FENE model, nano-confinement effects in the case of confining crystalline walls have been evaluated. An increase in $T_g$ and fragility both are found in the total film (thickness $\approx 18\sigma$), contrary to studies with force field walls that exhibit an increase in dynamics and subsequent depression in $T_g$. As shown in experiments$^{46,47}$, there is an increase in the time scale of relaxation near the wall relative the film center and to the bulk, producing the apparent upward shift in the glass transition temperature. Local dynamics near the wall are much slower than the center region of the film, requiring further study in order to encapsulate the full picture of the confinement effects.

After the local dynamics near the wall are determined, the problem of nano-confined flow will be addressed, because the short-FENE model is well suited for the task. This problem has been widely evaluated in very similar confinement geometry to the one used here$^{28}$. In these studies, understanding the validity of the oft-employed no-slip boundary condition is of the utmost importance; because interfacial dynamics can create an apparent slip condition when crystalline (or rough) walls are used in simulation and in experiment$^{39-45}$. Often the case of negative slip is seen in the flow of polymers, corresponding to an arrested region near the wall, which could be aptly described by the increased relaxation time imposed on the particles due to a surface roughness effect even in the “flat” crystalline wall case (contrasted by applications of periodic roughness$^{33}$). This is just one of many possible applications for the short-FENE model, and work has begun to validate the theory that increased equilibrium relaxation times near the interface could affect the non-equilibrium (steady-state) flow properties of a polymer melt. This could prove a useful tool in engineering new products and solutions by providing a link between the properties of a static film and its processing behavior.
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