Different Metrics for Connecting Mobility and Glassiness in Thin Films

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Abstract

Data continue to accrue indicating that experimental techniques may differ in their sensitivity to mobility and glassiness. In this work the Limited Mobility (LM) kinetic model is used to show that two metrics for tracking sample mobility yield quantitatively different results for the glass transition and mobile layer thickness in systems where free surfaces are present. Both LM metrics track the fraction of material that embodies mobile free volume; in one it is relative to that portion of the sample containing any kind (mobile and dormant) of free volume, and in the other it is relative to the overall sample. Without any kind of optimization, use of the latter metric leads to semi-quantitative agreement with experimental film results, both for the mobile layer thickness and the dependence of sample glass transition temperature on film thickness. Connecting the LM predictions with experiment also produces a semi-quantitative mapping between LM model length and temperature scales, and those of real systems.

Introduction

The glass transition temperature, T_g, and the segmental relaxation time, τ, are of notable interest in nanometrically thin polymer films, because their values may change relative to the bulk, depending on the nature of the interfaces. A number of experimental and theoretical methods have been applied to determine average and/or local properties of such thin film samples[1-23]. When considering changes in T_g and τ simultaneously, there are reports in the literature which show that the length scales over which T_g and τ are shifted from their bulk values can differ when measured via different techniques.[4,24-26] For example, fluorescence intensity measurements indicate that there is a T_g gradient that extends *tens* of nanometers into a PS free-standing film from the free surface,[12] whereas fluorescent probe reorientation[17-19] and nanoparticle embedment[4,6,25] studies report enhanced segmental mobility *at most* 10 nm away from the free surface. Other experimental techniques, e.g., dielectric relaxation and ellipsometry, have yielded analogous disagreements.[16,24,27] Based on these observations, some have suggested that there may exist a decoupling between τ and T_g.[4,24] It has also been proposed that different experimental measurements, such as the ones described above, may vary in their sensitivity to changes in τ and shifts in T_g,[26,28] thus accounting for some of the inconsistencies that have been reported in the literature.

We have recently developed a simple kinetic lattice approach, the Limited Mobility (LM) simulation model, to probe the role of mobility and free volume in the glass formation of bulk fluids and films.[29-32] The LM model differs from other kinetic lattice model approaches by decoupling free volume and mobility, allowing us to track their individual evolution as a fluid approaches its T_g. Using the LM model, we have characterized local T_g values and the region of enhanced mobility near the free surface of a film and, without any parameter optimization, have observed a semi-quantitative correspondence with available experimental data[28]. In this work, we investigate a different route to quantifying mobility and free volume in the LM model, and show that this new metric leads to a shift in predictions for T_g and mobile layer thickness for samples that incorporate a free surface. These results connect with observations that one choice of experimental technique may yield results that differ, relative to another, in their sensitivity to local mobility and glassiness. This may reflect differences in what contributes to the raw data and/or, as elaborated by Lipson and Milner,[33] differences that arise from how contributions from across the sample are averaged to give the overall reported result.

Limited Mobility Model Simulation

Here we briefly summarize the details of the LM model, referring the interested reader to the more detailed descriptions which can be found in Refs. 29-32, as well as in the Supplementary Information. Each lattice site in the LM model represents a fluid element in one of three possible states: "mobile", "dormant", or "dense", corresponding to three possible designations of relative mobility, as suggested by fluid simulations.[34,35] The first and third terms are self-explanatory; the second term represents fluid elements in which the potential for local motion is there, however, the free volume that exists is too diffusely distributed to be effective. The fraction of lattice sites occupied by each type of state is randomly assigned at the start so as to satisfy a chosen system average (e.g. 50% dense sites, 25% mobile sites, and 25% dormant sites) and then evolves over 5×10^5 Monte Carlo sweeps, according to attempted operations that represent the following microscopic physical processes: the translation of mobility throughout the fluid, the transition of free volume between a "mobile" state (i.e., a facilitator of "string-like" motion) to a "dormant" state (i.e., locally dispersed free volume), or visa-versa, and expansion/densification (which depends on temperature). It is important to note that the transition from a dormant to mobile state requires facilitation by a neighboring mobile site to be successful in the LM model. In order to simulate a film, boundary conditions are incorporated into the model such that a free surface is simulated by a lattice layer of permanently mobile sites, which can act as both a source and sink of mobility to sites in the adjacent lattice layer (with equal probabilities). A substrate is simulated by a lattice layer of permanently dense sites, which do not directly interact with sites in the adjacent lattice layer.

The LM model operations for the transitions between mobile to dormant site ("sleep" move) and dormant to mobile site ("wake up" move) are controlled by the model parameters k and k', respectively. [The parameter values can be combined into a ratio, k/k',[29,32] which is how they are treated in this work.] A bulk or film system in the LM model is characterized in its steady state for each choice of temperature and value of the ratio k/k'. In previous work on bulk fluids, Tito et al. proposed that the value of the ratio *k*/*k'* is related to the molecular characteristics of a fluid (e.g., chemical structure) that can influence its mobility and thus its bulk $T_{g.}$[30,32] For films, we have illustrated that the mobile layer thickness near a free surface in a film can be influenced by the value of the ratio *k*/*k'*.[29] In this work, we will restrict our investigation to a single value for the ratio *k*/*k'*, such that *k*/*k'* = 0.40/0.40 = 1.00, one that has been used in other work, e.g. Ref. 29.

In prior work, the relative amount of mobility in a bulk or film system was characterized by the steady state fraction of the number of sites containing *mobile* free volume, relative to those having either mobile or dormant free volume. This is denoted by the symbol: $\bar{\psi}$, and is given by:

$$\bar{\psi} = \frac{mobile}{mobile + dormant} \tag{1}$$

The tracking of mobility is key, since the value of T_g for a bulk or film sample in the LM model is defined according to a "glassy cut-off in mobility". In previous work,[29,30,32] the fraction of overall free volume that is mobile, $\bar{\psi}$, was used and the "cut-off" value for determining T_g was set to zero for bulk samples, and to 0.10 (approximately 1/*z*, the inverse lattice coordination number)[36] for film samples having a free surface. Choice of the latter value reflects a scenario in which each site has, on average, at least one mobile neighbor. Dipping below this cutoff leads to a system that will not exhibit mobility spanning across the sample, and will therefore be glassy. A finite cut-off value for mobility must be used to determine T_g when there is a free interface because in such a film system, this free surface acts as a temperature independent source and sink of mobility. The sample-averaged mobility will therefore never fall to zero. LM model initial studies on bulk systems showed vanishing mobility ($\bar{\psi}$ = 0) at a finite value of *T* that is controlled by the value of the ratio *k*/*k'*,[31] and that was the T_g identified in the original bulk studies. However, in subsequent work involving both bulk and film samples[29,30,32] we identified T_g as the temperature at which $\bar{\psi}$ = 0.10 in order to treat all systems consistently.

In this paper we introduce the steady state fraction of mobile sites out of the *total* number of sites, $\bar{f}$, as different metric for characterizing mobility using the LM model, where

$$\bar{f} = \frac{mobile}{mobile + dormant + dense} \tag{2}$$

The two metrics represent different weightings of mobility: $\bar{f}$ reflects the fraction of the overall sample that embodies mobile material, whereas $\bar{\psi}$ represents the fraction of less dense sample material that is mobile. We therefore define an analogous criterion for T_g corresponding to temperature at which $\bar{f}$ = 0.10. The rationale and implications for doing so are discussed below.

Results and Discussion

1. Mobility

First we will contrast the two approaches for quantifying mobility in the LM model: the steady state fraction of mobile sites, $\bar{f}$, and the steady state fraction of free volume that is mobile, $\bar{\psi}$, with respect to temperature. Figure 1 illustrates the change in the values of $\bar{f}$ (open squares) and $\bar{\psi}$ (filled squares) as a function of temperature for a bulk fluid (black) and a series of free-standing films of varying thickness (for all systems, *k* = *k'* = 0.40).

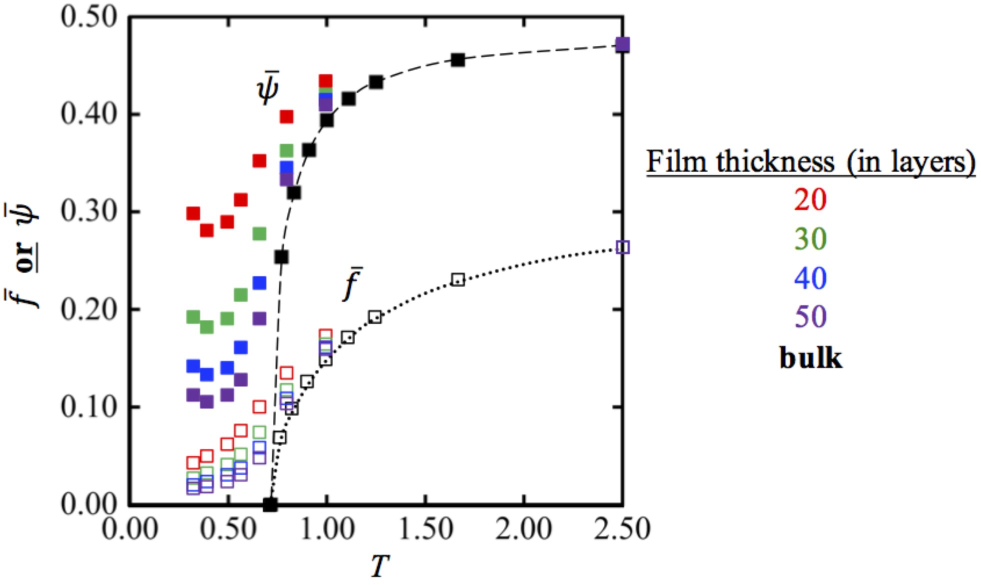

Figure 1: Change in the average fraction of mobile free volume, $\bar{\psi}$ (filled squares), and the average fraction of mobile sites, $\bar{f}$ (open squares), upon cooling a bulk fluid (black) and a series of free-standing films with *k* = *k'* = 0.40. The colored squares correspond to films of thickness 20 (red), 30 (green), 40 (blue), and 50 (purple) layers. Dashed lines are guides to the eye.

The results for the bulk fluid are shown in Figure 1 as open black squares (for $\bar{f}$) and filled black squares (for $\bar{\psi}$); each set is connected by a dashed line (guide to the eye). We observe the same *qualitative* bulk behavior for $\bar{f}$ and $\bar{\psi}$, i.e., their values are reduced as T decreases. At T = 0.71, $\bar{f}$ and $\bar{\psi}$ are both equal to zero (i.e., the fluid is kinetically arrested) [note: if $\bar{f}$ = 0 then $\bar{\psi}$ = 0, by definition]. For T > 0.71, the bulk values of $\bar{\psi}$ are larger than those for $\bar{f}$; $\bar{\psi}$ is a more "sensitive" metric of mobility. Using the "glassy cut-off in mobility", instead of zero mobility, as a route to T_g we find the $\bar{\psi}$ = 0.10 criterion yields a value of T_g = 0.73. However, the $\bar{f}$ = 0.10 criterion yields a value of T_g = 0.84. In the bulk system, requiring a minimum fraction of the entire sample to be mobile (via $\bar{f}$) is a slightly more demanding criterion (higher T_g) than applying that criterion (via $\bar{\psi}$) to the subset of material that is less dense (contains *either* dormant - red sites- or mobile - green sites - free volume).

Next, we turn to free-standing films, and Figure 1 indicates significant differences between not only the values, but also the temperature-dependent behavior of $\bar{\psi}$ and $\bar{f}$. For instance, $\bar{\psi}$ remains above the cutoff value of 0.10 for all of the free-standing films, which go from thicknesses of 20 (solid red squares), to 30 (solid green squares), to 40 (solid blue squares), and 50 (solid purple squares) layers, even as each film is cooled well below the bulk kinetic arrest temperature. None of these films can glassify according to the $\bar{\psi}$ = 0.10 criterion. Conversely there are experimental results (see Fig 3) of T_g values for supported films that are 20nm or thinner.[14] Additionally, note that the values of $\bar{\psi}$ begin to *increase* at low temperatures (T < 0.50), which suggests that the films are becoming *more mobile*. This counterintuitive result is a low temperature consequence of how $\bar{\psi}$ is defined. Recall that it only tracks mobile and dormant sites, and therefore does not reflect the dominance of dense sites, growing significantly in number, as T becomes low. Visualization of the simulation results shows clearly that at very low T the smaller numbers of mobile and dormant sites become exclusively restricted to the layers adjacent to the two free surfaces. The calculation of $\bar{\psi}$ does not account for the dramatically increasing importance of dense sites filling the interior of the film. In other words, when the mobile and dormant sites become sparse in the film interior, $\bar{\psi}$, becomes less effective at representing a total film average, and more of a reporting tool for the local mobility near the free surfaces. This has only became apparent as we have continued to push the limits of the LM model in simulating the low temperature behavior of samples in which interfaces play a major role. It highlights the importance of understanding what goes into a sample-averaged quantity, especially as the sample becomes increasingly inhomogeneous. This is not just an issue for simulations, but also should be a key consideration in comparing sample averaged results for mobility or glassines using different experimental techniques that may well track different 'reporters' (e.g. in terms of length or time scales) of behavior. For example, recent work in the experimental literature has referred to likely differences that result from using thermodynamic (e.g. calorimetric) versus dynamic (e.g. dielectric spectroscopy) techniques, [28,37] and this distinction has also been observed in several simulation studies.[38,39]

Figure 1 also shows that that $\bar{f}$ monotonically decreases toward zero as T decreases, without the anomalous upturn at very low T. For example, in a 20 layer film (red squares) at T = 0.50 the value of $\bar{f}$ = 0.06 while $\bar{\psi}$ = 0.29 at this temperature. According to $\bar{f}$, the film contains only 6% mobile sites, and has fallen below the glassy cutoff of $\bar{f}$ = 0.10. In contrast, the large $\bar{\psi}$ shows that even at low T there a significant fraction of the less dense material that is close to the free surfaces is still mobile. Both give information, however, the use of $\bar{f}$ avoids overweighting the influence of a small fraction of sites in calculating a sample averaged property.

In thinking about how a 'dormant' site and a 'mobile' site might manifest in a real, physical system, we can suggest a connection with the analysis in a recent perspective by White and Lipson[40] of total free volume in a fluid being comprised of physically distinct underlying contributions: e.g., “vibrational” free volume and “excess” free volume (the latter originating from imperfect packing as the melt solidifies). It seems reasonable that an increase in numbers of mobile sites with temperature would track with increasing “excess” free volume and particle mobility. Dormant sites are more likely to persist at lower T than mobile, so it seems feasible that the vibrational free volume survives in the dormant sites, while most (much) of the excess free volume does not.

We now turn to the localized region of enhanced mobility near a free surface in a film, which has been estimated to lie in the range 0 - 10 nm thic.k[2-4,6,13,17-21,25,41] Using the LM model, we have previously reported limited results characterizing the thickness of the mobile layer by tracking the number of lattice layers near a free surface whose *layer average* value is $\bar{\psi} > 0.05$.[29,30] In this work, however, we will track mobility using both $\bar{\psi}$ and $\bar{f}$, calculated layer-by-layer, with a cut-off value of 0.10 in order to be consistent with the "glassy cut-off" value for determining T_g.

Figure 2 illustrates the LM characterization of the mobile layer thickness as a function of $T/T_{g,bulk}$ for a 100 lattice layer thick substrate supported film (with $k = k' = 0.40$) at a T such that it is below the bulk glass transition.

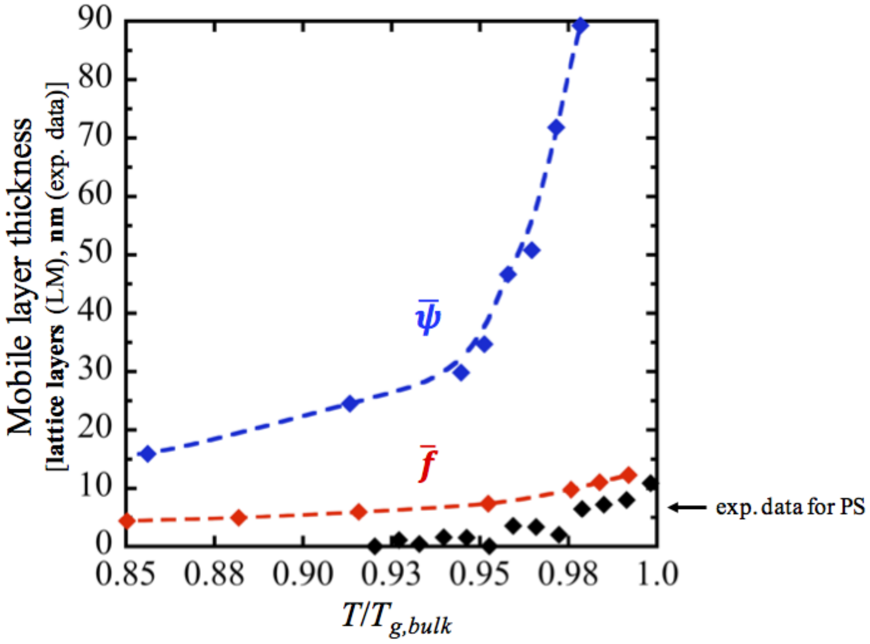

Figure 2: Comparison of the LM model results for the change in mobile layer thickness according to the $\bar{\psi}$ (blue diamonds) and $\bar{f}$ (red diamonds) criteria with respect to the reduced temperature $T/T_{g,bulk}$. Experimental results for 98 nm supported PS film (reproduced from Ref. 18) are also shown (black diamonds). Dashed lines are guides to the eye.

The LM model characterizations of the mobile layer thickness according to the $\bar{\psi}$ and $\bar{f}$ criteria that were described above are shown as blue diamonds and red diamonds, respectively, in Figure 2. Both sets of results indicate that the mobile layer thickness grows as a glassy film is heated from $T/T_{g,bulk} = 0.85$ to 1.0. Experimentally measured values obtained via a fluorescent probe reorientation technique for a 98 nm supported polystyrene (PS) film (MW = 160,000 kg/mol)[18] are also shown for the purpose of comparison. Note that we have not parameterized the LM model to specifically map to PS. Ref. 18 includes results for other supported film thicknesses and a free-standing PS film, with which our results are also consistent.

Figure 2 also makes clear that there is a notable difference between the thickness of the mobile layer when the characterization is based on $\bar{\psi}$ vs. $\bar{f}$. According to the $\bar{\psi}$ criterion, the mobile layer thickness grows from approximately 15 layers to 90 layers from $T/T_{g,bulk}$ = 0.85 to 0.98; i.e., the mobile layer grows to span nearly the entire film as $T_{g,bulk}$ is approached from below. However, the experimental measurements indicate that the mobile layer thickness grows from 0 to 6 nm over the same reduced temperature range[18], and the LM results using $\bar{f}$ turn out to be in semi-quantitative agreement with these data, without having optimized k/k' (or, indeed, changed its value at all from the first set of studies). Again, these results are consistent with a skewed sensitivity of $\bar{\psi}$ to small amounts of mobility. For example, consider a hypothetical lattice layer that contains 1 mobile site, 1 dormant site, and 62 dense sites. This configuration yields $\bar{\psi}$ = 1/2 (see equation 1), i.e., the layer would be categorized as "mobile", however, the value of $\bar{f}$ = 1/64 (see equation 2) for this layer, which is less than the glassy cutoff in mobility.

Looking more closely at the $\bar{f}$ results, we see that the mobile layer thickness grows from approximately 5 layers to 13 layers from $T/T_{g,bulk}$ = 0.85 to 0.98. Comparing this increase of 8 lattice layers with the experimental measurement showing growth of 6nm over the same reduced temperature range allows us to make a quantitative mapping between the length scale in the experimental system and the LM lattice model layer dimension : 1 lattice layer evidently corresponds to roughly 1 nm of this PS film. One conclusion from this analysis is that the thickness of the region of enhanced mobility near a free surface in a film as measured by fluorescent probe reorientation measurements, is more accurately captured using the LM model when mobility is characterized using $\bar{f}$. In addition, the mapping between experimental and model length scales allows us to draw quantitative conclusions regarding, for example, thickness changes, using the LM model as applied to PS films.

It is worth emphasizing again here that the distinction becomes important when tracking behavior near surfaces and/or near Tg, i.e. when the fractional mobility is approaching a cutoff value. Well away from surfaces, or in the bulk, the two metrics give similar results.

2. Glass Transition

In order to characterize a film average T_g we turn back to considering the film average mobility. In previous work, we used the "glassy cut-off" value of $\bar{\psi}$ = 0.10 for the film average mobility to determine the glass transition temperatures for films of varying thickness using the LM model.[29,30,32] We found that the film thickness dependent change in T_g characterized using the $\bar{\psi}$ criterion roughly mapped to the relevant film thickness and corresponding ΔT_g (= T_g - $T_{g,bulk}$) value ranges measured experimentally for PS and poly(methyl methacrylate) (PMMA).[29,30] In Figure 3, we illustrate how the mapping between the LM model results for free-standing films (with $k = k'$ = 0.40) and experimental measurements changes when using the $\bar{f}$ = 0.10 "glassy cut-off" criterion to characterize film average T_g values.

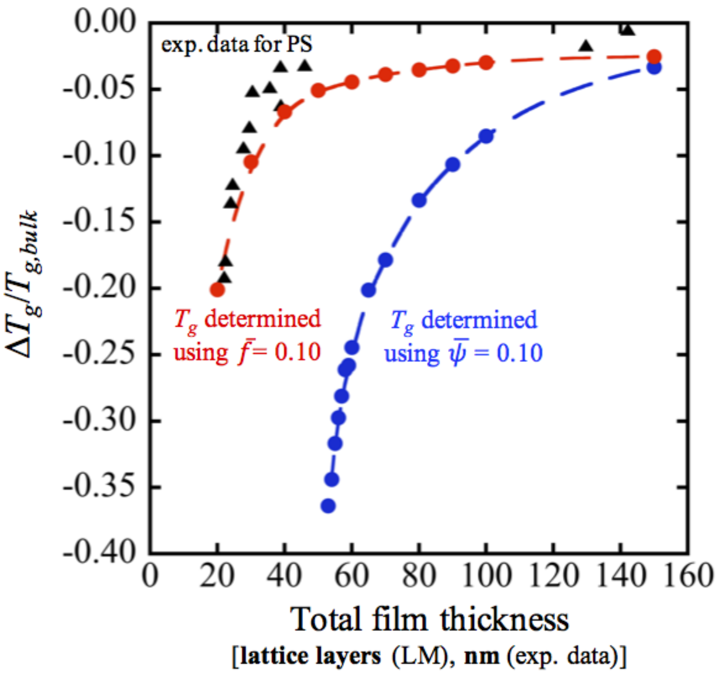

Figure 3: Thickness-dependent values for $\Delta T_g/T_{g,bulk}$ for free-standing films. The red and blue points correspond to the LM model results, where the $\bar{f}$ = 0.10 criterion (red) and $\bar{\psi}$ = 0.10 criterion (blue) were applied. The black triangles correspond to Brillouin light scattering measurements of T_g for a freely standing polystyrene (PS) film (M_n = 116 000 g/mol) reproduced from Ref. 14. Dashed lines are guides to the eye.

Compared to the Brillouin light scattering measurements of T_g (black triangles) shown in Figure 3, the values of $\Delta T_g/T_{g,bulk}$ determined according to the $\bar{\psi}$ = 0.10 criterion (reproduced from

Ref. 27) indicate that the simulated film T_g values are more strongly suppressed from the bulk T_g than the real films. Indeed, a T_g cannot even be determined for a film less than ~55 lattice layers thick because, according to $\bar{\psi}$, the film could reduce its fraction of mobile sites enough, even at low temperatures, to become glassy. As noted above, this is due to the sensitivity of $\bar{\psi}$ to the small amount of mobility that continues to enter from the free surface even when the film is primarily composed of dense sites. While quantitative comparison with MD results is difficult we also note that recent studies[38,39] on ultrathin PS found that both static (density) and dynamic metrics showed clear shifts to lower T_g for the films, relative to bulk.

Figure 3 also shows that using the LM model with the $\bar{f}$ = 0.10 criterion yields values of $\Delta T_g/T_{g,bulk}$ for simulated free-standing films that are both very different from the $\bar{\psi}$ -based predictions (especially for thicknesses less than 100 nm) and also in strong agreement with the experimental results for the free-standing PS films (as for all the LM results, $k = k' = 0.4$). . In this case the LM values of $\Delta T_g/T_{g,bulk}$ range from approximately -0.20 to 0 as film thickness increases from 20 to 150 lattice layers, which roughly matches the corresponding experimental results for films ranging in thickness from 20 to 150 nm[14]. This suggests a length scale mapping of 1 lattice layer to roughly 1 nm of the experimental film. Also, note that once the film becomes thicker than roughly 150 nm the two criteria yield the same result.

In addition to the film average T_g, there have been recent theoretical and experimental efforts to probe local T_g values in films reported in the literature[1,5,11,12,22]. For example, MD and coarse grain simulations were used by Khare and Mani[42] and Hsu et al.[43], respectively, to characterize the change in the local T_g of a film as a function of distance from an interface (e.g., polymer-free surface, polymer-polymer, and polymer-substrate). Experimentally, local T_g values have been probed by positioning a 'reporting' layer in a sample. Recent work has explored both soft and hard confinement, [23] but here we focus on results using a fluorescent labeled layer at a chosen position in a film of the same (but unlabeled) material. For example, Torkelson et al.[12] used a 14 nm thick pyrene labeled layer at the free surface of free-standing PS films in order to determine the local T_g change as the thickness of the under-layer was varied. In Ref. 29, we used the LM model to conduct an analogous study in which we characterized the local mobility over a 30 lattice layer thick region at the free surface of simulated free-standing films (with $k = k' =$

0.40), and calculated the *local* T_g value of this region based on the $\bar{\psi}$ = 0.10 criterion. From our analysis, we concluded that the LM model results showed the same *qualitative* behavior that was reported by Torkelson et al.[12]

However, from the above results it is clear that the $\bar{f}$ = 0.10 criterion will provide a different *quantitative* picture of glass transition suppression, especially considering that the sample being monitored represents a thin slice near a free surface. The results shown Figure 4 test predictions using the LM $\bar{f}$ metric against analogous experimental data[12], and also provide a test for our proposed mapping of 1 nm = 1 lattice layer. For this study we constructed a reporting layer thickness of 15 lattice layers to compare with experimental results reported by Torkelson et al.[12] that correspond to a 14 nm thick reporting layer (open green circles). The experimental polymer was PS; simulation parameters remain at k = k' = 0.40.

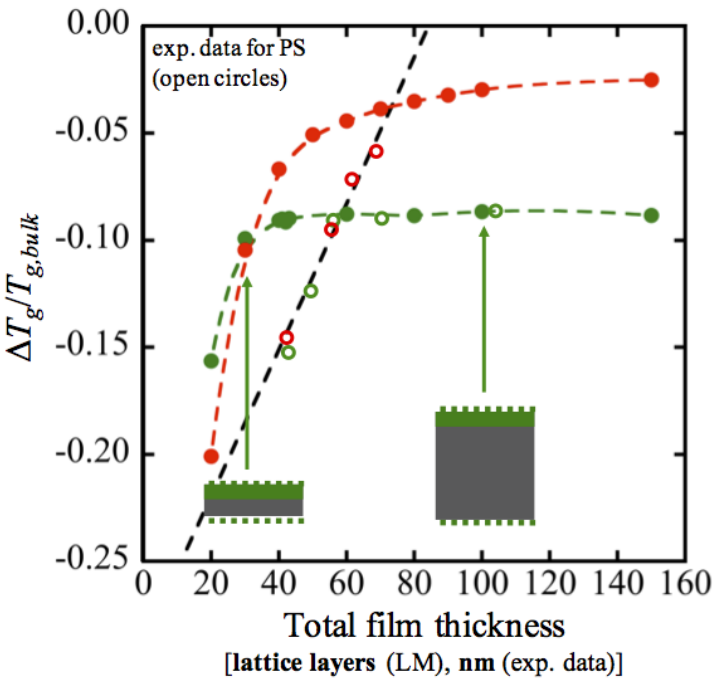

Figure 4: LM model results for the change in $\Delta T_g/T_{g,bulk}$ for a free surface reporting layer (filled green circles) of 15 lattice layers thick in a free-standing film with respect to varying the total film thickness [film average results are shown for the purpose of comparison (filled red circles)]. Experimental results are reproduced from Ref. 12, which correspond to a 14 nm pyrene-labeled PS reporting layer (M_n = 805 000 g/mol) at the free surface of a free-standing film (open green circles); film average results (open red circles) are also shown. Inset cartoons illustrate the relative thickness of the reporting layer to the total film thickness for the LM model results. Dashed lines are guides to the eye.

The red points in Figure 4 correspond to the whole-film average $\Delta T_g/T_{g,bulk}$ values using the $\bar{f}$ = 0.10 criterion (filled red circles) and the experimental data (open red circles). The LM results are the same as depicted in Figure 3, since the system is a freestanding film and the k,k' values have not changed. The experimental results in Figure 4 are taken from the same study as those for the labeled reporting layer[12], in order for there to be internal consistency. Both simulation and experiment show the expected trend: there is an overall film thickness below which the average glass transition temperature of the system begins to diminish significantly. The experimental data suggest this happens at around 70 nm, while the LM results begin to plummet at a film thickness of about 40 lattice layers.

Next we turn to main results of interest, the experimental (open green circles) and LM (filled green circles) surface reporting layer measurements for the free-standing films. The LM simulations involve a reporting layer that is 15 lattice layers thick, while the experimental analogue is one of 14 nm. Both sets of results illustrate that the local T_g of the free surface reporting layer is suppressed from that of the bulk T_g value. In both cases T_g is constant as the total film thickness decreases from about 150 nm to 40 nm (experimental) or from 150 to 20 lattice layers (LM). For the experimental study, once the overall film becomes less than 54 nm thick (at which point the 14 nm reporting layer sits on top of an underlayer that is 40 nm thick) a stronger T_g suppression is observed, comparable to that of the film average T_g value. Torkelson et al.[12] suggested that this behavior is the result of the underlayer becoming thin enough so that mobility propagates across the film from the *other* (unlabeled*)* free surface, which thus perturbs the reporting layer's local T_g. The LM results also demonstrate that when the underlayer becomes thin enough, in this case about 25 lattice layers, mobility propagating in from the second free surface enhances the effect and the layer T_g diminishes rapidly, and becomes comparable to that for the whole-film average.

Finally, the results shown in this figure are reasonably consistent with the suggested mapping of roughly 1 lattice layer : 1 nm length scale we observed between our LM model calculations and experimental measurements of the mobile layer thickness using the $\bar{f}$ = 0.10 criterion.

Conclusions

In this work, we use the Limited Mobility (LM) simulation model to compare and test different metrics for tracking mobility. In the LM model free volume and mobility are not synonymous, as there are two kinds of sites that contain free volume: mobile and dormant. One LM metric corresponds to tracking that fraction of total free volume that is mobile, $\bar{\psi}$. In contrast, $\bar{f}$ represents the fraction of mobile sites relative to *all* other sites in the system, and thus is a better representation of the global average.

We show that tracking sample mobility using different metrics may change the assessment of mobile layer thickness, as well as the *quantitative* prediction for the glass transition temperature; these effects are most significant when free surfaces are present. In discussing the results we draw an analogy with the ways in which different experimental techniques may vary in their sensitivity to mobility.[26,28,37]

Using both metrics for mobility in the LM model, we characterized: the size of the region of enhanced mobility near the free surface of a film, T_g values for free-standing films of varying thickness, and the local T_g value of a reporting layer located near the surface of a free-standing film. We tested our results against experimental data on polystyrene films, and found excellent agreement using $\bar{f}$ as the metric, without optimization of LM parameters. Using $\bar{\psi}$ yields results that share some of those qualitative features, with notably less quantitative agreement.

At low temperatures, even when a free surface is present, the *sample wide* fraction of free volume is small. However, the presence of the free surface continues to serve as a source and a sink of *mobile* free volume. The result is that in the presence of a free surface $\bar{\psi}$ over weights mobility due to surface effects, and this is reflected in its estimate of the global average of mobility (or lack thereof) in the system. Since a cutoff value in mobility is used to judge the both the glass transition and mobile layer thickness, a quantitative disagreement between the two metrics is likely to lead to different quantitative results, for example, in the thickness dependence of T_g for a freestanding film.

Comparison of simulation and experiment also revealed that using $\bar{f}$ the LM model can be mapped to the relevant length scales (one LM lattice length being roughly equivalent to one nanometer) and T_g changes measured experimentally for these systems[12,14,18]. We conclude that $\bar{f}$ represents a practical and insightful quantifier of sample mobility in systems where interfaces play an important role, a feature that will be important as we apply the LM model to study more complicated morphologies.

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Notes

There are no conflicts to declare.

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Connecting Mobility and Glassiness in Thin Films

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