Local and average glass transitions
in polymer thin films

Jane E. G. Lipson,* † and Scott T. Milner*, ‡

Department of Chemistry, Dartmouth College, and Department of Chemical Engineering, The
Pennsylvania State University

E-mail: jane.e.g.lipson@dartmouth.edu; stm9@psu.edu

Abstract

In the companion paper to this we presented a quantitative theory for the suppression of the
glass transition in a thin polymer film. Our Delayed Glassification (DG) model follows a pro-
posal by de Gennes that free volume can be transmitted from surface to film interior via kinks
transported along molecular strands or loops. In this paper we use the DG model to predict
the effects of molecular weight and film thickness on the film-averaged glass transition for a
polystyrene sample. Our predictions for both freestanding and supported films of polystyrene
illustrate that the DG model is able to account for some, but not all, of the experimental trends.
This leads us to confront a number of issues, including how to average local glass transitions
to yield a sample value, as well as how to rationalize the nature of the molecular weight de-
pendence for transitions in the thinnest freestanding films.

*Department of Chemistry, Dartmouth College
†Department of Chemical Engineering, The Pennsylvania State University
1 Introduction

Experimental evidence for the dramatic suppression of the glass transition of a polymeric film in the neighborhood of a free surface has been available for close to a decade, and yet no quantitative, predictive model has been developed to account for these results. In the companion paper to this work we presented a theoretical approach having generational roots in suggestions made some years ago by de Gennes.\(^1,2\) The underlying physical picture is that chains at the surface can pick up kinks of free volume that may translate along the chain into the film and help to plasticize layers which are relatively (on the scale of tens of nanometers) remote from the free volume source, e.g. at the air interface. The source is also the sink, and so the kinks travel along polymeric loops. Translation of a kink along a loop takes time, and will therefore only help to lower the local glass transition (and thereby delay glassification) relative to the bulk if the travel time is less than the bulk relaxation time at the bulk glass transition temperature.

There are several essential elements of our Delayed Glassification (DG) model. We assume that the local segmental relaxation times obey the well-known Williams-Landel-Ferry (WLF) temperature dependence,\(^3\) which leads to that same functional dependence on \(T\) for \(N^*(T)\), the longest effective loop length. We also use Gaussian statistics for the loops in order to obtain a relatively simple result for the probability that a segment a distance \(z\) away from the interface is on a fast loop. For this latter analysis we consider two scenarios: that a loop is made slow by a single slow segment, or, that the cumulative effect of moderately sluggish segments may cause a loop to become slow. The two cases differ noticeably in mathematical complexity, but marginally in resulting predictions. We therefore proceed here with the simpler of the two pictures, that of slowness being induced via the existence of a slow segment.

Development of the DG model also requires a condition for the transition to local glassiness, i.e. a value for the critical probability, \(p_c\). For this we applied the condition used in our earlier percolation work,\(^4\) viz. that coordinated slowing down of a local region required at least some limited connection between the site in question and neighboring sites. We settled on a value for \(p_c\) of the inverse of a local 'coordination' number, however, we noted then, and repeat here, that
our results are not particularly sensitive to this choice. In this paper we apply the DG model, for the case of both finite and infinite molecular weight polymer, to predict the local glass transition as a function of film thickness for both a semi-infinite supported and a freestanding film. In the semi-infinite case the only interface is that of the free surface; the effect of substrate is not included.

While it would be interesting to test our predictions for local \( T_g \) against experimental data, such results are not yet available, although some experiments come closer than others (as will be discussed below). In order to compare directly with experiment we shall have to consider how to translate from a set of local \( T_g \) values to a prediction for the expected \( T_g \) of a film having some experimentally manageable thickness. Before undertaking such a comparison it is useful to consider what the experimental measurements track in the course of detecting a glass transition.

A variety of techniques, some of which were noted in Paper 1, have been used to probe the thickness dependence of the glass transition in a thin film. For example, measurements such as dielectric relaxation\(^5,6\) and Brillouin scattering\(^7-9\) are sensitive to slowing down of the local dynamics as the glass transition is approached. Signature responses from local modes sum over the sample being probed in order to produce an overall signal. Another class of techniques yields information about the change in height, or density, of a sample as a function of temperature, exploiting the fact that the thermal expansion coefficient changes dramatically as a system goes from melt to glass. Methods such as ellipsometry\(^8,10-18\) and x-ray reflectivity\(^10,19-21\) fall into this class, and in all cases the measured signal represents an average over the total sample thickness.

Also in this category is a fluorescence labeling technique developed by Torkelson and coworkers\(^22-28\) (see also references in\(^24\)), whereby selectively labeled layers of interest in a thin film may serve to report on the glass transition. The fluorescence probes, which are uniformly distributed throughout the layer of interest, emit a cumulative signal which is sensitive to local changes in density. The experiment therefore essentially detects a change in sample height, or thickness, with changing temperature, averaged over the thickness of the reporting layer. The result is a layer-averaged glass transition, with the added control of being able to label the thickness and position of the layer within the film.
As noted above, experimental measurements of $T_g$ for a film of a given thickness represent an average. Even the fluorescence labeling results report a value which is averaged, albeit only over the labeled portion of the sample. Figure 5 of the companion paper to this work illustrates how the local glass transition may be expected to vary within a film of a given thickness for a freestanding film. The simplest route to an average $T_g$ would be to integrate over the relevant profile and then divide by the total thickness. The result is that each local transition is weighted equally, and is what we refer to as the 'democratic average'.

While both conceptually and arithmetically simple, the democratic average does not capture what the experimental data show for freestanding films, which is a very dramatic reduction of film $T_g$ from the bulk value as film thickness is decreased. For example, the study by Dalnoki-Veress et al.\textsuperscript{29} on freestanding films of polystyrene (PS) having molecular weights ranging between $3.50 \times 10^5$ g/mol and $9.00 \times 10^6$ g/mol shows that for a sample of $7.67 \times 10^5$ g/mol the film $T_g$ drops from the bulk by 60K as the sample thickness decreases from 65nm to 40nm. For a sample of $6.68 \times 10^6$ g/mol the drop in transition temperature is 80K as the film thickness changes from roughly 85nm to 65nm. Overall, the data reveal that film $T_g$ values decrease abruptly from the bulk value at thicknesses which have a rather weak molecular weight dependence. In addition, the rate at which $T_g$ drops with film thickness is, itself, a weak function of molecular weight, with the most dramatic shifts being associated with the largest molecular weights.

In contrast, regardless of the underlying model for local $T_g$ as a function of film thickness, the result of performing a democratic average is that the overall film $T_g$ is doomed to approach the bulk value with a $1/h$ dependence, which is a significantly slower approach than experimental data show. We therefore pursue an alternative, suggested by our simple treatment of the transition between glass and melt for layers plasticized by the presence of a free surface.

As a final introductory point we raise the issue of molecular weight dependence for the case of supported films. There appears to be a fairly general consensus\textsuperscript{24} that even down to extremely low molecular weights (on the order of $10^4$ g/mol) there is no evidence of molecular weight dependence. A modest reading the literature does suggest a number of general observations. For
example, the bulk glass transition temperatures appear to be achieved for films having thickness around 75 nm, regardless of the molecular weight of the sample.\textsuperscript{24} It is also clear that the presence of a substrate has significant experimental impact, in that dramatic suppression of the glass transition only becomes evident for extremely thin films - those having thicknesses below about 20 nm. Films thicker than this only show shifts in $T_g$ of about 5K or less relative to their eventual bulk value. A complicating issue is that there also appears to be a rather significant dispersion of $T_g$ values when results using different techniques from different labs are compared,\textsuperscript{24} such that the uncertainty in $T_g$ at any given film thickness is likely to be at least 5K. It therefore becomes difficult to draw firm conclusions about possible molecular weight effects for films of modest thickness when the precision is on the order of the effect. On the other hand, the thinnest supported films, i.e. the ones which show the most dramatic effects, have the complication of being under the influence of the substrates on which they are supported. Given that our model describes semi-infinite films, focusing on the effects of the free surface and not accounting for an underlying support, it becomes problematic to draw firm quantitative conclusions regarding issues such as molecular weight dependence. The one set of experimental data which provides a real opportunity for comparison has been collected for only one molecular weight. This means that a true test of our model results for semi-infinite films is yet to come, as we discuss further below.

The rest of the paper is divided as follows: In the next section we discuss how the model is used to create the theoretical equivalent of an experimental lineshape, such as are often shown when ellipsometry measurements are carried out. In section 3 we discuss different possible routes to identifying the glass transition for a slice of film, and strategies for reporting an averaged $T_g$. In sections 4 and 5 we present results for semi-infinite and freestanding films. Finally, section 6 is devoted to our summary and conclusions.
2 Local lineshape

The experiments described above measure the total film thickness as a function of temperature. The total film thickness is the sum of the thicknesses of each differential slice. The slices will in general have different local glass transition temperatures, and thus will contract by different amounts as the film is cooled.

We envision dividing the film into differential slices of equal mass per area, or equivalently of equal height $dz$ at the bulk glass transition. (Above the bulk glass transition, the density everywhere in a freestanding film is equal, as no part of the film has yet become glassy.) We take as our reference length scale the root mean square radius of gyration of the longest loop, $N^\ast(T^b_g)$, which is effective at the bulk $T^b_g$. For our model calculations we choose a finite molecular weight equal to $N^\ast$.

We may then write the change in total film thickness $\Delta h(T)$ as an integral over the relative change in local film thickness $\delta h(z, T)$, as

$$\Delta h(T) = \int_0^h dz \delta h(z, T)$$

in which $h$ is the total film thickness at $T_g$.

For small thickness changes, $\delta h(z, T)$ is given by the ratio of the change in local density $\delta \rho(z, T)$ to the density $\rho_g$ at the bulk glass transition,

$$\delta h(z, T) = -\delta \rho(z, T)/\rho_g$$

We model the local relative changes in thickness $\delta h(z, T)$ phenomenologically, as follows. By definition, $\delta h(z, T^b_g)$ vanishes (we measure thickness relative to its value at $T^b_g$). Above the bulk glass transition, we are in the melt state, in which all portions of the film have the same thermal expansion coefficient $\alpha_m$, assumed to be independent of temperature for simplicity.

At a temperature $T_g(z)$ at or below $T^b_g$, a differential slice at $z$ undergoes its local glass transition,
calculated in paper I. Below \( T_g(z) \), the slice is glassy, falling out of complete thermal equilibrium. A glassy slice loses some formerly accessible vibrational modes, and its thermal expansion coefficient is reduced to some smaller value \( \alpha_g \). We assume each glassy slice to have the same \( \alpha_g \), regardless of the value of \( T_g(z) \) (i.e., how suppressed the glass transition was for the slice, or how close to the free surface).

It remains to specify how \( \delta h(z, T) \) changes between \( T_{g}^b \) and \( T_g(z) \), in the “plasticized state”, made molten by the action of loops transporting kinks. First, we assume that all plasticized slices have the same density at a given temperature. Second, we assume that the thermal expansion coefficient of a slice at \( z \) is a smooth function of \( T \) above \( T_g(z) \); in particular, there is no break in slope of \( \delta h(z, T) \) at the bulk transition for a plasticized slice (for which \( T_g(z) \) is distinctly less than \( T_{g}^b \)). So we may write

\[
\delta h(z, T) = \begin{cases} 
\alpha_m(T - T_{g}^b) & T \geq T_{g}^b \\
\delta h(T) & T_g(z) < T < T_{g}^b \\
\alpha_g(T - T_g(z)) + \delta h(T_g(z)) & T \leq T_g(z) 
\end{cases}
\]

In the above, \( \delta h(T) \) is a “lineshape function” we must specify. It must have slope \( \alpha_m \) at \( T_g \) for continuity with the melt. And, it must have slope \( \alpha_g \) at \( T_0 \), the minimum temperature at which we may still have any plasticized region. Our choice for the function \( \delta h(T) \) determines how the thermal expansion coefficient of the plasticized material decreases with temperature. This decrease corresponds to a gradual withdrawal of some of the vibrational modes that would have become inaccessible at \( T_{g}^b \), but were preserved by the plasticizing action of the loops. Here we assume a smooth linear transition of \( \alpha(T) \) between values \( \alpha_m \) at \( T_g \) and \( \alpha_g \) at \( T_0 \). This differs from the cartoon proposed by de Gennes,\textsuperscript{1,2} who posited that the plasticized state would have a constant thermal expansion coefficient \( \alpha_p \), with a value intermediate between \( \alpha_m \) and \( \alpha_p \). That simplified model would however lead to a sharp transition at \( T_{g}^b \), at which the thermal expansion coefficient jumped from \( \alpha_m \) to \( \alpha_p \) throughout the film. Such a transition has not been reported, which is part of the motivation for our proposal.
3 Locating the transition

As illustrated in the companion paper to this, different slices in a film undergo their local glass transition at different temperatures. These local glass transitions are presumed sharp, with a break in slope of $\delta h(T)$ at $T_g(z)$. However, the change in total film thickness $\Delta h(T)$ will not display a sharp glass transition, because the constituent slices have their local transitions at different temperatures $T_g(z)$.

![Graph showing the change in film thickness with temperature](image)

Figure 1: Representative curves for $\delta h(z, T)$ (with break in slope, dashed below $T_g(z)$), for a series of thin slabs contributing to the overall $\Delta h(T)$ (solid curve).

In Figure 1 we illustrate how local transitions for a series of slices within a film combine to yield a prediction for the dependence of overall film thickness on temperature. Each of the dashed lines shows thickness versus temperature for a single slice. The progression of dashed lines from top to bottom illustrates the effect of slice position, ranging from deep in the film (topmost) to a slice at or near the surface (bottom most). Note that the curve for the deepest slice has the most marked change in slope at the transition. This slice is positioned deep enough that the temperature needed to melt the material is near that of the bulk glass transition. Conversely, the bottom dashed curve
in the set exhibits the weakest transition, in the sense of slope change, at the lowest temperature. This is associated with a slice close to the surface, where the local glass transition has been deeply depressed.

A straightforward averaging of the contributions from each, equivalent, slice would yield a single curve. Three examples of such curves are shown in Figure 2, which illustrates the results for three choices of the overall film of thickness, \( h \). This plot is analogous to what an experimentalist would obtain on three such samples using, for example, ellipsometry or fluorescence methods. In analogy with the experimental analysis, we must now specify how a single transition temperature is to be assigned for a freestanding film of thickness \( h \). Experimentalists commonly fix a transition temperature over some range of \( T \), by drawing a tangent to the data on each end of the data set and finding the intersection point of the two tangents. The question arises: how wide in \( T \) should the data set be taken, and where should the tangents be drawn?

![Figure 2](image)

**Figure 2:** Representative curves for \( \Delta h(T) \), together with tangents at \( T = T_0 \) and \( T = T_g \) (dashed), and markers for “mid-slope” points. Curves offset for clarity. Values of \( h/h^* \) equal to 0.1, 0.6, 1.5.

Informed by the present model, the logical places to draw the two tangents are 1) at the bulk glass transition \( T_{gb} \), where the entire film must have the melt thermal expansion coefficient \( \alpha_m \);
and 2) at the Vogel temperature $T_0^3$ for the slip motion, where the entire film must have the glass thermal expansion coefficient $\alpha_g$. Of course, for the experimenter the lower tangent poses a problem, because we do not know a priori where $T_0$ is; $T_0$ for slip motion need not be the same as the value for the bulk glass transition. Still, the essence of our tangent prescription is to take the upper tangent where the thermal expansion coefficient matches the known value $\alpha_m$ for the bulk melt, and take the lower tangent where the thermal expansion coefficient matches the known value $\alpha_g$ for the bulk glass.

In the theory, of course, it is straightforward to implement this procedure for locating the crossing point of the two tangents. Below $T_0$, Eqns. (1) and (3) give a linear behavior for $\Delta h(T)$, namely

$$\Delta h(T) = \int_0^h dz \left( \delta h(T_g(z)) + \alpha_g(T - T_g(z)) \right)$$

(A4)

Above $T_g^b$ we again have a linear result, $\Delta h(T) = h\alpha_m(T - T_g^b)$. Thus above $T_g^b$ and below $T_0$, the function $\Delta h(T)$ is its own tangent. Equating these two expressions determines the crossing point $T_{g,tan}$ of the tangents. We define $\Delta T_{g,tan}(h)$ equal to $T_{g,tan}(h) - T_g^b$, the shift of the apparent glass transition relative to bulk.

A modest amount of algebra reveals that determination of the glass transition via the intersection of the two tangents described above is identically equivalent to taking the unweighted, 'democratic', average of the local glass transitions in the film. In other words, averaging the transition over the total set of slices within the film yields the exact result of the limiting tangents associated with the melt and sub-Vogel temperature glass.

In Figure 2 we show the three sets of tangents. That associated with each trace above the melt $T_g$ has been drawn in red, and is the same in all three cases. The tangent associated with the trace below $T_0$ has the same slope in each case, of course, but occurs in a different position, reflecting the different temperature at which the overall film went glassy. The three different intersection points of the sets of tangents would therefore be the estimates using this approach for the overall film $T_g$ reported for each of three the respective thicknesses. Three arrows are also indicated in the figure,
An important distinction can be made between films thick enough to have an interior region that is not plasticized (and therefore becomes glassy at $T_{bg}$), and films thin enough that all portions of the film are plasticized to some extent. We call the former case “sandwich” films, with the “meat” being the interior unplasticized region and the “bread” the plasticized portions on either face of the film. For sandwich films, only the “bread” regions contribute to the integral the average $\Delta T_g, tan$ of Eqn. (5):

$$\Delta T_{g, tan}(h) = \frac{2}{h} \int_0^{h^*} dz \Delta T_g(z) W(\Delta T_g(z))$$

(5)

Here $h^*$ is the maximum depth into the film that is ever plasticized, i.e., $T_g(h^*)$ equals $T_{gb}$.

Now consider the dependence of $\Delta T_{g, tan}(h)$ defined by Eqn. (5) on total film thickness $h$. We of course expect that for sufficiently thick films, the average transition temperature $T_{g, tan}(h)$ should approach the bulk transition $T_{gb}$, hence $\Delta T_{g, tan}(h)$ should approach zero. However, it is apparent from Eqn. (5) that $\Delta T_{g, tan}(h)$ approaches zero slowly, as $1/h$. Different choices for the shape of $\delta h(T)$ and hence the weighting factors $W(\Delta T_g(z))$ may reduce the coefficient of this $1/h$ approach, but the coefficient will never be zero. So, for example, a plot against film thickness of $T_g$ values obtained as illustrated in Figure 2, from the intersection points of the tangent lines, would show a clear $1/h$ dependence.

In contrast, the reported values for glass transition temperatures from ellipsometry experiments as a function of film thickness show a sharp crossover to the bulk $T_{gb}$ value, not a slow $1/h$ approach. Note however that the experimenters do not systematically report their lineshapes, nor do they draw their tangents at a standard temperature; it may well be possible to get rather different results for the transition temperature depending on where the tangents are drawn.

The route just described for determining the averaged $T_g$ of a film as a function of thickness therefore has several disadvantages. We thus seek an alternative, albeit still well-defined, route to the averaged transition. We note in passing the implication that the result will no longer represent a ‘democratic’ weighting of the local transitions.

Recall that we chose a linear transition in thermal expansion coefficient between bulk melt and...
glass values. A rather straightforward alternative route is therefore to identify the glass transition temperature as that associated with a tangent to the curve having slope exactly halfway between the melt and the glass slopes. Results for the three sample curves in Figure 2 are indicated by solid arrows; the locations of the transitions appear to be close to what the eye would choose as the most noticeable 'break' in the trace.

4 Results for semi-infinite films

Figure 3 displays representative curves for $\Delta h(T)$, for a set of freestanding films made from a sample of infinite molecular weight polystyrene (PS). In this case there is only one length scale in the problem, viz. the longest possible active loop, which is the loop length, $N^* = N^*(T_{b_g}^b)$ at $T_{b_g}^b$. As in Paper 1, we choose $N^*$ to be $2.0 \times 10^6 \text{ g/mol}$, which sets the limit for the longest effective loop length in an infinite molecular weight sample. This particular choice is motivated by observing that for PS of extremely high molecular weight (certainly by $9.1 \times 10^6 \text{ g/mol}$) the bulk glass transition is achieved for films having thicknesses of roughly 95 nm and greater. As noted in the figure caption, the set of film thicknesses studied, expressed in reduced units, ranges from 0.1 to 1.5. The reduction parameter is the root mean square radius of gyration of a loop of length $N^*$ which, for the choice listed above, is a length of 38.0 nm. Thus, the total film thicknesses represented in Figure 3 range from 3.8 nm to 57.0 nm.

As described above, we identify the transition as occurring at the temperature associated with a tangent line having a slope halfway between that of the glassy and melt regions. The set of resulting transition temperatures is indicated in the figure by black arrows.

In Figure 4 we map the results of Figure 3 to create a plot for the infinite molecular weight sample of the shift in $T_g(z)$ from the bulk value of 373K as a function of relative film thickness. Once again, the abscissa is shown in reduced units, where the reduction parameter is the root-mean-squared radius of gyration of a chain of length $N^*(T_{b_g}^b)$, chosen here to be $2.0 \times 10^6 \text{ g/mol}$. Thus the abscissa represents film thicknesses out to 57.0 nm, at which point $h = 1.5h^*$. As the figure
Figure 3: Family of curves for semi-infinite film top labeled layer \( \Delta h(T) \) versus temperature, for \( h/h^* = 0.1, 0.3, \ldots 1.5 \) and chain length \( N = N^* \). Other parameters as in main text (\( c = 8, T_0 = 273K, \alpha_g/\alpha_m = 0.25 \)).

shows, the theoretical predictions are reasonable both for the degree of \( T_g \) depression, as well as for the relative length scale over which it occurs. Equally important, the model results exhibit a notable drop in \( T_g \) for films having thickness less than about 52 nm, with a subsequent shift in temperature of roughly 30K over a change in film thickness of only 30 nm. This is qualitatively consistent with experimental observations,\(^ {24} \) and distinctly different than the slower, \( 1/h \)-like drift which is the result of the so-called ‘democratic averaging’ process discussed previously.

In semi-infinite films only one free surface is present, and there are no interactions with a substrate. Experimental implementation of this arrangement has been realized in the work of Torkelson et al. (see Fig. 2 of\(^ {23} \)), which includes results for a labeled surface reporting layer of variable thickness resting on a 'silent’ (i.e. unlabeled) very thick (240 - 270 nm) layer of the same polymer loaded onto a substrate. Observed differences from the bulk glass transition can thus be attributed solely to the influence of the film/air interface. Similarly, our model for the semi-infinite film reflects only the presence of one free surface.
Figure 4: Glass transition temperature $T_g$ versus $h/h^*$, as inferred by “mid-slope” criterion, corresponding to results of Figure 3.

Although the theoretical result for the probability that a segment is a particular distance away from the surface differs in the semi-infinite case, relative to that for the finite film (cf equations 12 and 13 in paper I), the model predicts a similar sensitivity to molecular weight. In Figure 5 we show the effect of changing molecular weight on the range and extent of the $T_g$ shift; as the figure caption indicates, the molecular weights are in reduced units, with the reduction parameter being the value of $N^*$. Choosing the value of $N^*$ to be $2.0 \times 10^6$ g/mol would therefore translate the results in Figure 5 to be associated with molecular weights, from left to right, of $4.0 \times 10^5$, $8.0 \times 10^5$, $1.2 \times 10^6$, $1.6 \times 10^6$, and $2.0 \times 10^6$ g/mol. For the two largest molecular weight model samples the limits of plasticization have essentially been reached, and moving to still higher molecular weights would produce negligible change.

Experimental data points illustrating the whole-film $T_g$ shift in supported films are somewhat scattered, as Fig. 1 in the recent paper by Torkelson et al. illustrates.24 However, the cumulative results generally support the notion that PS thin films on silicon oxide substrates exhibit thickness-related shifts in the glass transition that are essentially independent of molecular weight. We note,
though, that the right experiments have not yet been done to determine whether this insensitivity to molecular weight is evident even when only a slice of the film adjacent to the free surface is reporting. In this sense our model predictions have yet to be tested.

Figure 5: Glass transition temperature $T_g$ versus labeled top layer thickness $h/h^*$ for semi-infinite films, for a family of different molecular weights $N/N^* = 0.2, 0.4, 0.6, 0.8, 1.0$. Other parameters as in main text ($c = 8$, $T_0 = 273K$, $\alpha_g/\alpha_m = 0.25$).

5 Results for freestanding films

As noted in the Introduction, experimental results illustrating the effect of film thickness on the glass transition of freestanding films of varying molecular weight show striking trends\textsuperscript{29,30} (see in particular Fig. 4 of Dalnoki-Veress et al. 2001 [DV]). In Figure 6, which is the analogue of results for the semi-infinite case given in Figure 3, the shift in glass transition as a function of total film thickness for a free-standing PS film of infinite molecular weight is indicated by the series of arrows. This set of temperature-thickness results represents what would be obtained as the limiting set of points in Figure 7 which, in fact, shows results for a series of finite molecules weights. As in Figure 7, the molecular weights are scaled relative to the value of $N^*$, such that the
choices represented in the figure correspond (using $2.0 \times 10^6$ for $N^*$) to values of (from left to right) $4.0 \times 10^5, 8.0 \times 10^5, 1.2 \times 10^6, 1.6 \times 10^6, \text{and } 2.0 \times 10^6$ g/mol.

![Figure 6: Family of curves for freestanding film $\Delta h(T)$ versus temperature, for $h/h^* = 0.2, 0.6, \ldots 3.4$ and chain length $N = N^*$. Other parameters as in main text ($c = 8, T_0 = 273K, \alpha_g/\alpha_m = 0.25$).](image)

There are both notable similarities and differences in comparing the model results to those of experiment. Before detailing these, we emphasize that we have not tried to optimize agreement with experiment in generating the results of Figure 7; the PS-related parameters are the same as those used in producing results for the semi-infinite films of varying molecular weights.

Even given comparable shifts in temperature over comparable length scales it is clear that there are conceptual differences between the model predictions and the DV set of experimental data.\textsuperscript{29} According to the theory, plasticization in sufficiently thin films becomes independent of molecular weight. For example, the model predicts that a freestanding film of 20 nm or 30 nm thickness will be plasticized equivalently for a sample of, say, 300,000 g/mol as for one of 3,000,000 g/mol. This means that our 'fan' of molecular-weight dependent lines coalesce at a point associated with small length and low temperature. This does not match the DV data\textsuperscript{29} which fan in the opposite
Figure 7: Glass transition temperature $T_g$ versus freestanding film thickness $h/h^*$, for a family of different molecular weights $N/N^* = 0.2, 0.4, 0.6, 0.8, 1.0$. Other parameters as in main text ($c = 8$, $T_0 = 273K$, $\alpha_g/\alpha_m = 0.25$).

direction, the lines coalescing at a putative temperature higher than the bulk $T_g$, and distance larger than the thickest film for which experimental $T_g$ suppression is observed.

The pattern in the experimental data is impressively clear, yet we remain puzzled by the evident sensitivity of the film results at low length scales to the molecular weight of the sample. For example, from the DV data\textsuperscript{29} we see that a film of 40nm thick shows a $T_g$ suppression of about 40K for a sample of $5.75 \times 10^5$ g/mol, compared to a 70K shift for a sample of $1.25 \times 10^6$ g/mol. In both cases, the film is significantly thicker than the root-mean-squared radius of gyration, which would be roughly 20 nm for the former and 30 nm for the latter. In addition, considering the thicker samples in the study, why does the film $T_g$ drop so much more precipitously from the bulk value for the highest molecular weight samples, relative to the behavior for the lowest molecular weight? Answers remain elusive, however, we can certainly conclude that accounting for plasticization through transmission of free volume along chain loops does not capture these particular aspects of whatever physical phenomena the data reflect.
6 Summary and conclusions

More than a dozen years have passed since the initial reports of a shift in the polymeric glass transition temperature for material in a thin film, relative to the bulk. Early experiments focused on supported films, however, much of the recent research has targeted freestanding films. The range in configurations — from examining multicomponent layers, to the effect of embedded nanoparticles — as well as the increasing breadth of experimental techniques have resulted in the creation of a field which is more blessed by data than by understanding. This paper, along with the preceding one, as well as recent (unrelated) work which develops a percolation treatment for the local glass transition in supported thin films, represent our own efforts to bridge the rapidly widening gap between experimental results and theoretical insight.

Our earlier study on supported thin films, which was the first paper to generate model results for the profile of local glass transitions, lead us to conclude that a percolation treatment was capable of capturing the effect of an attractive substrate on both the local and averaged glass transition. On the other hand the predictions, while reflecting the independence of sample molecular weight on experimental results, also made clear that the depression of $T_g$ observed close to the surface could not be accounted for solely by a reduction in the number of percolating paths linking isolated glassy clusters to the globally glassified layer adjacent to the substrate.

In this two-paper study we create (in paper I) and implement (here) the Delayed Glassification (DG) model, which brings to life in a clear and substantive way the notion, first suggested by de Gennes, that a free surface may serve as source and sink for segmental-sized ’kinks’ of free volume. Using this ’slip’ mechanism in our DG model, the kinks, created and destroyed at the film-surface interface, propagate into film by traveling along polymeric loops. A loop that is too long is no longer effective at helping to plasticize the film; the ’effective’ loop length is temperature-dependent. One parameter in the model is $N^*$, the limiting effective loop length which is still active at the bulk $T_g$. At lower temperatures we have assumed a WLF-like form for $N^*(T)$, thereby introducing two additional parameters: the associated energy parameter, $A$, and limiting temperature, $T_0$. Finally, we use an exponential distribution to account for the effect of finite molecular weight.
This modifies the probability that a loop may be active, since a kink encountering a chain end will no longer be able to propagate.

The DG model accounts for some, but not all, of the physics revealed through experiment. We find a dramatic drop in the glass transition, relative to the bulk value as film thickness diminishes. Both the rate at which the glass transition is suppressed as a function of thickness, as well as the critical thickness at which this occurs, depends on molecular weight. At high enough molecular weights the effects saturate, and further increases have no additional effect. We depart from experiment in finding that molecular weight differences vanish for ultrathin films, where the extent of \( T_g \) suppression becomes molecular weight independent. We also find that the suppression of the glass transition for semi-infinite films is dependent on the molecular weight of the sample in a way which is analogous to that of free-standing films. These predictions remain to be tested, as current data on \( T_g \) suppression in the presence of a single air interface involve films supported by a substrate.

In summary, we hope that these results are provocative enough to generate new data, and look forward to revisiting the challenges of understanding these systems as new experimental evidence of the physics involved is revealed.

References


