When Does a Glass Transition Temperature Not Signify a Glass Transition?

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ABSTRACT: We present a simple model that links enhanced mobility at the free surface to the dilatometric glass transition temperature, T_g in thin films. The model shows that what is typically measured as a dilatometric T_g, characterized by the hallmark "kink" in the plot of film thickness versus temperature, only represents the dynamics of an infinitesimally thin layer of the sample. In other words, the measured dilatometric T_g value in thin films is no longer a good reporter of the dynamics. Calculations based on the model are found to agree with a vast body of thin film T_g measurements. While mathematically simple, the model contains all the necessary physics of a near surface layer with enhanced dynamics and a length scale over which the surface dynamics monotonically varies from surface enhanced to bulk-like. The model demonstrates that the typical dilatometric measurement of the glass transition is not necessarily a real glass transition.
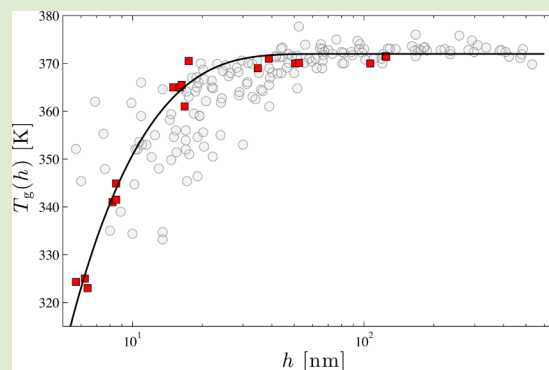
The glass transition temperature, T_g, is often used as a semicomprehensive description of the dynamics of glass forming systems. This single temperature is essentially a distillation of the entire temperature dependent relaxation times of the system. While the glass transition is widely accepted to be a kinetic phenomenon, the rapid change of dynamics that happens as the sample is cooled through T_g gives rise to various physical manifestations (such as near discontinuities in the heat capacity or thermal expansion) which are often used as a probe for the change in dynamics. For this reason the T_g in bulk materials is an excellent reporter of the material dynamics. The expectation that this correlation between such quantities as thermal expansion and the material dynamics is maintained for thin films is a key component of the controversy that has accompanied measurements of T_g in thin polymer films.[1−4]

The idea of a dynamical length scale in glasses, and the difficulty in measuring it, has been a strong motivating factor for measurements of T_g in highly confined systems. Thin films are an ideal geometry, and polymeric materials (due to their metastability in thin films and ease of finding materials that avoid crystallization) are an ideal class of materials. For these reasons, the measurement of the glass transition temperature in thin polymer films has become an area of intense study, and at times, contradiction. Currently, there is general consensus that for films thinner than $h \sim 20$ nm prepared from the most commonly studied polymer, polystyrene, the measured T_g decreases from that of the bulk, T_g(bulk), with decreasing thickness. The observations of much larger T_g reductions in free-standing (no substrate) films compared to supported films reinforces the suggestion that the free surface contributes to the measured T_g reductions.[5−7] While the lack of a definitive theory for glass formation even in bulk materials limits the ability to describe thin film T_g measurements, a number of models have been proposed.[8−10] One thing these models have in common is that the measured T_g value is directly related to the average material dynamics. That is, the T_g value from the theory is a real glass transition temperature and for temperatures $T > T_g$, the material is liquid-like, and for $T < T_g$, the material is glassy. These theories are at odds with some qualitative and quantitative observations in thin films. For example, free-standing polymer films can be held for many hours at temperatures 10s of degrees above their measured dilatometric T_g values (as long as the measured $T_g < T_g$(bulk)) without any of the hole formation that would be expected of even the most viscous polymer melt.[1] Measurements of segmental mobility in free-standing films show that only a fraction of the thin film has measurable dynamics when the temperature is below the bulk glass transition temperature, T_g(bulk) value.[11] This is in agreement with the gradients in measured T_g value near the free surface.[12]

A starting point to understand the observations in thin films should start with an understanding of the properties of the near free surface region, and many recent studies have shown and

quantified evidence for enhanced mobility near the free surface.[11,13−17] The size of this region of enhanced dynamics is on the order of a few nanometers. One of us has recently suggested that a convenient way to parametrize the depth dependent dynamics is through the rheological temperature R.[18] It is important to note that the rheological temperature is not an actual temperature, but a parametrization of the dynamics. R is simply the temperature a bulk system would have in order to exhibit the same dynamics. That is, if a polystyrene film were held at 330 K, and the near surface region was more mobile with dynamics corresponding to a bulk sample at 380 K, then T = 330 K, while R = 380 K. Furthermore, a region that is in the melt state would be characterized as $R > T_g$(bulk), while a glassy region has $R < T_g$(bulk). The key advantage of this parametrization of the dynamics over techniques where we might try to define the relaxation times as a function of distance from the free surface is that it does not require any a priori understanding of the bulk dynamics at the temperature range of interest below T_g(bulk). In other words, we can characterize a system as having some value of $R < T_g$ without necessarily knowing what the measured relaxation time is at that temperature. We note that since this is not a temperature but rather a parametrization of dynamics, we can have different R values for different types of motions. This R value could be measurement-dependent (for example, it could depend on the frequency of an a.c. measurement, or cooling rate in calorimetric or ellipsometric studies) and is the temperature the bulk system would have to be in order to have the same properties (relaxation time, modulus, etc.) as those measured for any portion of the system with the same thermal history. In other words, the rheological temperature describes any fraction of a system with position-dependent dynamics in terms of the average dynamics of that same material in bulk. Thus, a particular region in a dynamically inhomogenous sample that has a faster dynamics than the bulk would have a higher rheological temperature than the actual temperature of the system. Simply stated, enhanced dynamics is characterized by $R > T$, while dynamics that is more sluggish than the bulk has $R < T$. It is important to note the distinction between the local R value defined above versus a local T_g value where local enhanced dynamics would be defined by $T_g < T_g$(bulk).

Let us consider the case of a film on a noninteracting substrate, though what is to follow can easily be adapted to free-standing films, other geometries (e.g., colloidal particles), or systems with strongly interacting substrates. We assume that near the free surface of a glassy polymer the local rheological temperature $R(z)$, varies monotonically as the distance from the free surface, z, as shown schematically in Figure 1. Immediately at the free surface, $R(0) = R_s$, and then deep within the film, the bulk value must be recovered and $R(\infty) = T$. There is a length scale $\xi(T)$ over which the dynamics changes from surface-like to bulk-like. There is evidence to suggest[17,20,21] that this $\xi(T)$ may be the same or proportional to the dynamical correlation length often discussed for glass forming systems. Following the evidence from experimental measurements which indicate a weak temperature dependence of the nanodeformation evolution on the surface of polystyrene,[22] we first consider the case where R_s is temperature-independent. Other experiments suggest a more significant temperature dependence[16] of surface properties that will be discussed later.
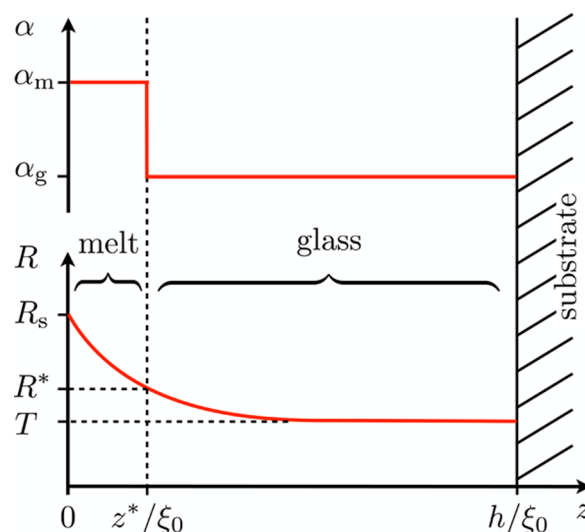

Figure 1. Schematic diagram of the expansion coefficient α and rheological temperature R in a film supported on a substrate. The film is bound by the free surface at $z = 0$ and the substrate at $z = h/\xi_0$.

We consider the rheological temperature as a function of distance from the free surface. If the length scale from surface-like to bulk-like behavior is characterized by $\xi(T)$, we can write

$$R(z) = T + (R_s - T)f(z/\xi(T)) \tag{1}$$

where $f(z/\xi(T))$ is any function that is monotonically decreasing with its argument. As mentioned previously, both R_s and, hence, $R(z)$ could depend on the time scale of the dynamics that are probed by the measurement (it is not a requirement that all dynamics exhibit enhancement at the free surface). Furthermore, we have the boundary conditions at the surface, $f(0) = 1$, and in the bulk, $f(\infty) = 0$ (see Figure 1). As in ref 18, we consider the case where an experiment probes a particular time scale. That time scale, in turn, will correspond to a particular rheological cutoff R^*. For thermal expansion measurements, R^* is then the lowest temperature where a bulk system would be in the melt state. Since we are considering the case where R^* defines the transition from melt to glass, $R^* = T_g$(bulk). A sample with heterogeneous dynamics may have a portion with $R > R^*$ that is in the melt, while the remaining portion is in the glassy state. If an experiment probes relaxations faster than those corresponding to R^*, then we define the size of the region that will be probed in that experiment as $z^*(T)$.[18] Thus,

$$z^*(T) = \xi(T)f^{-1}\left(\frac{R^* - T}{R_s - T}\right) \tag{2}$$

For the particular case of a dilatometric measurement, the surface region of a film from 0 to z^* has the expansivity of the polymer melt α_m, while the rest of the sample expands as the glass, α_g. We note that this is a two-state approximation (see Figure 1) of the real temperature dependence of the thermal expansivity in the bulk, but is necessary to allow a closed form solution, and certainly suffices for our purposes here. The net effect of this approximation is that a continuously varying $\xi(T)$ results in a simple two layer model for the expansivity: a film with thickness h will then have a melt region with thickness z^* and a glassy layer of thickness $h - z^*$. We emphasize that we are not constructing a two layer model, as in refs 7 and 19. Instead we allow for a continuous distribution of dynamics

through the z dependence of R. It is only when we restrict the thermal expansion to have one of two discrete values, α_m or α_g, that a layer model naturally results. The temperature-dependent thermal expansivity of the entire film is then given as

$$\alpha = [\alpha_m z^* + \alpha_g(h - z^*)]/h \qquad (3)$$

For a dilatometric measurement of T_g, the temperature is varied and typically the transition is taken as the midpoint where $\alpha = (\alpha_g + \alpha_m)/2$. Thus, at the measured dilatometric glass transition, the system satisfies the condition that $z^*(T) = h/2$. Note that replacing the word expansivity by heat capacity would allow the same argument to be made for calorimetric measurements carried out at the same cooling rate as typical dilatometric studies.

At the thin film glass transition $T_g(h)$, and making use of eq 2,

$$\frac{h}{2\xi(T)} = f^{-1}\left(\frac{T_g(\text{bulk}) - T_g(h)}{R_s - T_g(h)}\right) \qquad (4)$$

which simplifies to

$$T_g(h) = R_s + \frac{T_g(\text{bulk}) - R_s}{1 - f\left[h/2\xi(T_g(h))\right]} \qquad (5)$$

We note that this expression is still completely general, and in order to calculate $T_g(h)$, we need to specify the function f that describes the spatial extent of the enhanced surface dynamics. We consider the simple example where f decreases exponentially as z increases, $f(z/\xi(T)) = \exp(-z/\xi(T))$. We stress that the qualitative results obtained here do not depend on this choice of functional form. Using eq 5, if we include the simplifying assumption that $\xi(T) = \xi_0$ (i.e., temperature-independent), we can now write an explicit expression for $T_g(h)$

$$\frac{T_g(h) - T_g(\text{bulk})}{R_s - T_g(\text{bulk})} = \frac{1}{1 - \exp(h/2\xi_0)} \qquad (6)$$

Figure 2 is a plot of the functional form of eq 6 and shows that if the rheological temperature of the free surface is higher than that of the bulk (i.e., $R_s - T_g(\text{bulk}) > 0$), then the measured glass transition of a thin supported film decreases with decreasing film thickness, consistent with the vast majority of experiments. Figure 2 is notable in that it describes an apparent reduction in the dilatometric T_g value at a particular h value even though only a layer with vanishingly small thickness would actually have it's dynamics described by that T_g value. This idea is consistent with the layer-by-layer T_g studies of ref 12, though we have not calculated layer-by-layer T_g values for direct comparisons with those measurements. In other words, the measured T_g value is essentially uncoupled from the film dynamics. At T_g, a bulk sample would be near equilibrium in its entirety on the time scale of the experiment, but in our model at T_g for a thin film, only half of the film is in equilibrium, while the remainder is in the glassy state. This demonstrates that the same dilatometric measure leads to different dynamical scenarios in thin films and bulk materials.

Figure 3 shows data that represents a large body of the thickness-dependent T_g values in the literature for supported polystyrene films.[1,3] This data shows a great deal of scatter, and it is not clear that fitting to data with such large scatter is the best approach. As an alternative, we fit to a subset of T_g data
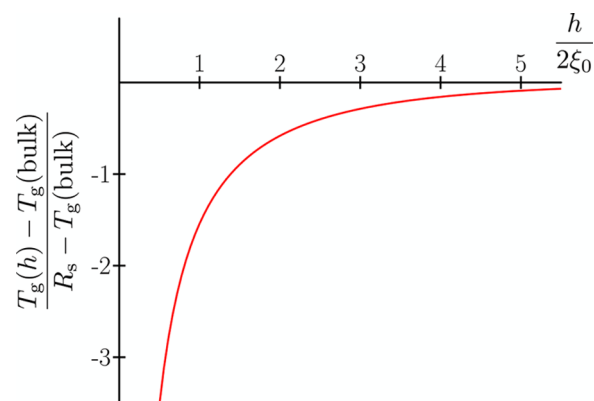

Figure 2. Normalized change in the glass transition as a function of the normalized film thickness as given by eq 6.
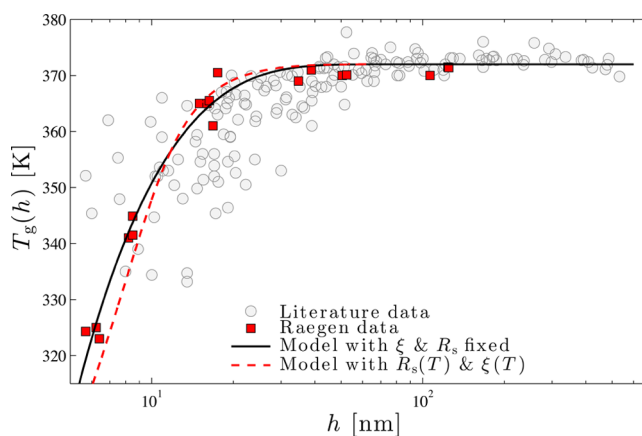

Figure 3. $T_g(h)$ using the model described in the text with both constant (solid line) and variable (dashed line) values for R_s and ξ. Best fit parameters are given in the text.

where the annealing conditions and atmosphere have been carefully controlled and documented.[23] These data are shown as the solid squares in Figure 3. Also shown as lines in this figure are calculations based on eq 6 for two cases of $\xi(T)$. In the first case (solid line), we use a constant value of ξ_0 and R_s and fit the equation to the data to obtain $R_s = 435$ K and $\xi_0 = 3.6$ nm. We can see from Figure 3 that this very simple approach provides an excellent description of not only the data from ref 23, but the entire body of literature data shown.

Despite this agreement, we need to examine other possibilities. In particular, we have assumed that R_s is independent of temperature. This means that the relaxation time of segments at the free surface is independent of temperature. This is rather unphysical, as there must be some slowing down with decreasing temperature. To obtain a more physically reasonable temperature-dependent expression for R_s requires an expression for the temperature-dependent relaxation time in bulk materials near the bulk T_g value. Since there are studies that suggest a high surface mobility in the temperature range of interest,[16,22] a reasonable approach would be to use the bulk Vogel−Fulcher−Tamman (VFT) expression for the relaxation times near the bulk T_g to get a temperature-dependent rheological surface temperature. The VFT equation is given by $\tau \sim \exp[B/(T - T_0)]$, with B the activation temperature and T_0 the Vogel temperature. In the simplest case that the surface relaxation can be described as a simple activated process[14,15] $\tau \sim \exp(E_s/T)$, where E_s is an activation barrier

associated with surface relaxations. By equating the surface relaxation dynamics at some temperature T to that of the bulk at some temperature R_s, we obtain the surface rheological temperature: $B/(R_s - T_0) = E_s/T$, where E_s is the activation barrier for the surface process. With this, the apparent rheological surface temperature R_s is given by

$$R_s(T) = T_0 + \frac{BT}{E_s} \qquad (7)$$

We must also consider that there is reasonable evidence to suggest that the length scale $\xi(T)$, which describes how the dynamic perturbation due to the free surface extends into the rest of the film, has a temperature dependence. In particular there have been studies that suggest a length scale that is consistent with cooperative approaches to glass transition dynamics.[7,17] A reasonable first order approach would be to do a series expansion about the bulk T_g value by writing

$$\xi(T) = a_0 + a_1[T_g(\text{bulk}) - T] \qquad (8)$$

where $a_0 = \xi(T_g)$. We do not determine these parameters by fitting to T_g data but rather by considering the results from Roth and co-workers for $\xi(T)$.[17] In particular, we use $a_0 = 4$ nm and $a_1 = 0.2$ nm/K as a reasonable description of the length scales obtained in ref 17. This approach enables a single parameter fit to the data for E_s. The fit of eq 6 with R_s and $\xi(T)$ given by eqs 7 and 8 is shown in Figure 3 by the dashed line and is also an excellent description of the data. We obtain the best fit value of $E_s = 1.0 \times 10^4$ K with the VFT parameters $T_0 = 327$ K and $B = 1878$ K taken from ref 24. Given that this approach is an effective description of the data, a picture emerges that is consistent with all T_g values in Figure 3, the $\xi(T)$ values in refs 7 and 17 and the surface behavior of refs 16 and 22. Even though we have not improved on the already impressive fit to the data, the fact that we have now used parameters that agree with independently determined literature values, makes this is a satisfying level of agreement. The value obtained for E_s is in the range of activation energies found in measurements of slow dynamics in thin films[25] and at $T \sim T_g$ suggests a surface relaxation rate $\sim 4 \times 10^5$ times that of the bulk relaxation rate. We note that the use of other sets of VFT parameters in the literature lead to similar values of E_s.

We can use eq 3 for the temperature dependent thermal expansivity of the film in order to simulate dilatometric data, $h(T)$. Figure 4 shows $h(T)$ for 5, 10, and 20 nm films normalized to their thickness at 370 K using the parameters required to obtain the dashed line in Figure (3) and with illustrative values of $\alpha_g = 2 \times 10^{-4}$ K^{-1} and $\alpha_m = 1 \times 10^{-3}$ K^{-1}. Note the familiar kink in the thickness versus temperature curve that is used to characterize T_g in dilatometric measurements. In addition to the lower T_g values for thinner films (as shown in Figure (3)) we see that thin films have a broader transition which may appear as a lower transition contrast than thick films. The reason for the lower contrast is that even though $T < T_g$ some fraction of the film contributes a melt-like expansivity as follows from eq 3. This result is qualitatively similar to that measured in ref 26. It is important to note that, consistent with observations, these effects will only be observable for very thin films. For example, using eq 6 and the values $R_s = 435$ K and $\xi = 3.6$ nm as above, a 1 μm thick film, will exhibit an immeasurable T_g reduction of $\sim 10^{-59}$ K.

We stress that we are not claiming to provide an explanation for all reduced T_g values in the literature. In particular, we do
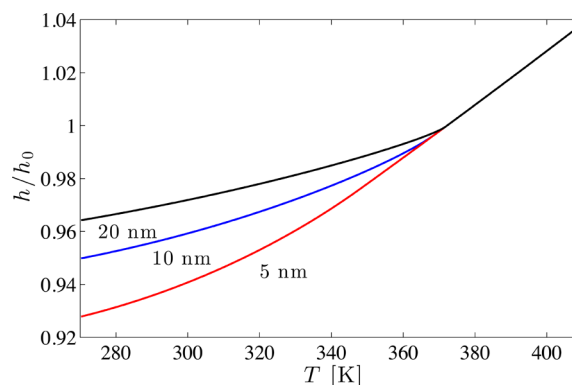

Figure 4. Simulation of $h(T)$ for films with thicknesses of 5, 10, and 20 nm, normalized at $T_g(\text{bulk}) = 372$ K. E_s and $\xi(T)$, as described in the text. Note that the contrast in the slopes and position of the "kink" in the curves decreases with decreasing film thickness.

not attempt to provide an explanation for the very large M_w reductions in apparent T_g measured in free-standing films. The recent discussion of two different mechanisms for mobility in thin films from Roth and co-workers[17,27] suggests that the simple inclusion of a second mechanism for transferring excess surface mobility with length scale ξ_2 which depends on the molecular size, could suffice to model the data for free-standing films. We also note that there are some contradictory experimental observations that measure T_g reductions significantly different from the data shown in Figure 3. While the model is consistent with the bulk of the measurements, clearly the model can not describe those contradictions.

It is important to note the differences between our approach and approaches where the T_g value is strongly coupled with the material dynamics.[8−10] Our approach describes a measured dilatometric T_g value which is a convolution of enhanced surface dynamics, and the length scale for that effect penetrating into the film. For the case leading to the dashed line in Figure 3, the film thickness dependent "apparent" T_g value is determined only by properties of the bulk system and the E_s parameter characterizing the surface mobility. The most important consequence is that, while we can calculate a $T_g(h)$ for a thin film from $T_g(\text{bulk})$, E_s, and ξ, the measured T_g value can not be used by itself to make a strong quantitative inference about the material dynamics.

We have shown that the proposed model is consistent with a vast literature data on $T_g(h)$,[1,3] the contrast of the transition,[26] and the fact that thin films can be stable to hole formation above their apparent T_g.[1] We now discuss further observations in the literature and how they are supported in our simple model. In comparing different experiments we have to keep in mind that the R_s depends on the dynamics being probed in a particular experiment. In other words, R_s should also be considered as a function of the experimental probe time τ, just as bulk measurements of T_g depend on kinetics. If, as it has been suggested by recent experiments,[25] only slow dynamics at the free surface are enhanced, then $R_s(\tau) > T$ for large τ but for smaller τ (faster dynamics probed) $R_s(\tau) \sim T$. This reasonable qualification allows the same model to be used to describe all dilatometric and calorimetric measurements of T_g in thin polystyrene films. Furthermore, experiments have suggested a $h \rightarrow 2h$ mapping when comparing the apparent T_g between supported and free-standing films.[7] This observation is accounted for by the fact that in our model the calculated T_g

will depend on the volume fraction of near surface material consistent with the $h \rightarrow 2h$ mapping. The model presents a very simple argument incorporating only an enhanced surface mobility that diminishes as one traverses into the sample. The reduced T_g values are (by design) consistent with the length scales presented in the aging results of ref 17 as well as to studies of enhanced surface mobility.[16,22]

In summary we have shown that a simple parametrization of excess surface mobility characterized by the rheological temperature at the interface which extends into the film with some characteristic length scale $\xi(T)$ can be used to describe essentially all of the measured dilatometric T_g values presented in the literature in the past 20 years. The model achieves this while maintaining consistency with the temperature dependence of dynamical correlation length in bulk glasses. The success in this construction to explain measured T_g values suggests that there is a decoupling between dilatometric T_g and the material dynamics and that the glass transition temperature in thin films no longer has the strong correlation to dynamics characteristic of bulk materials; in other words, the model demonstrates that the typical dilatometric measurement of the glass transition may not correspond to a real glass transition.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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