



Why we need to look beyond the glass transition temperature to characterize the dynamics of thin supported polymer films

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There is significant variation in the reported magnitude and even the sign of T_g shifts in thin polymer films with nominally the same chemistry, film thickness, and supporting substrate. The implicit assumption is that methods used to estimate T_g in bulk materials are relevant for inferring dynamic changes in thin films. To test the validity of this assumption, we perform molecular simulations of a coarse-grained polymer melt supported on an attractive substrate. As observed in many experiments, we find that T_g based on thermodynamic criteria (temperature dependence of film height or enthalpy) decreases with decreasing film thickness, regardless of the polymer–substrate interaction strength ϵ . In contrast, we find that T_g based on a dynamic criterion (relaxation of the dynamic structure factor) also decreases with decreasing thickness when ϵ is relatively weak, but T_g increases when ϵ exceeds the polymer–polymer interaction strength. We show that these qualitatively different trends in T_g reflect differing sensitivities to the mobility gradient across the film. Apparently, the slowly relaxing polymer segments in the substrate region make the largest contribution to the shift of T_g in the dynamic measurement, but this part of the film contributes less to the thermodynamic estimate of T_g . Our results emphasize the limitations of using T_g to infer changes in the dynamics of polymer thin films. However, we show that the thermodynamic and dynamic estimates of T_g can be combined to predict local changes in T_g near the substrate, providing a simple method to infer information about the mobility gradient.

thin polymer film | glass transition | film dynamics

Ultrathin polymer films have important practical applications, ranging from flexible integrated circuits (1) to tissue engineering (2). These films are often spin coated on solid substrates, including silicon, silica, and aluminum, and the properties of the resulting polymer films are often found to deviate from those of the corresponding bulk material (3–20). Understanding the origin of thermodynamic and dynamic changes in “ultrathin” films is important not only for the applications of these materials, but also for our understanding of the fundamental nature of glass formation. The most common metric to quantify the dynamic changes in these films is the glass transition temperature T_g . Many studies have been devoted to how the substrate (21–25), film thickness (15, 26), molecular mass (4, 27), or physical aging (8, 28–30) affects the apparent film T_g . It is generally appreciated that the “free” surface layer of the polymer film, i.e., the polymer–air interface, exhibits enhanced dynamics; changes to dynamics near the substrate vary, depending on the strength of polymer–substrate interactions, and strongly attractive substrates are expected to slow dynamics. As the film thickness decreases, the effects of the interfaces become increasingly large. The theoretical challenge is to understand how competing interfacial and confinement effects give rise to changes in observed T_g values, as well as the sensitivity of various methods to the gradient of molecular relaxation across the film.

Despite the substantial literature on T_g changes in polymer films, there are wide variations in the magnitude, and even whether T_g should decrease or increase, for a given film. For example, polystyrene, one of the most commonly studied polymer films, shows a decreasing T_g with decreasing film thickness for many different experimental methods, sample preparation procedures, and the physical nature of the supporting substrate. Many of these experiments use T_g measurements from a thermodynamic approach, e.g., ellipsometry (measuring the change of film thickness with temperature) or differential scanning calorimetry (measuring specific heat as a function of temperature). On the other hand, inelastic neutron-scattering measurements (31–33) probing the mean-square molecular displacement $\langle u^2 \rangle$ on a picosecond timescale (fast β relaxation time), a quantity directly related to the structural relaxation time at a segmental scale (34), indicate an upward shift of the T_g for the same film for which a downward shift T_g is indicated by the thermodynamics measurements. A summary of the wide range of reported results among many experimental methods is illustrated in figure 1 of Kremer et al. (35); we also recommend the recent review article on polymer films by Priestley et al. (36) which discusses the large disparities between T_g estimates based on quasi-thermodynamic measurements vs. dynamic measurements. These conflicting estimates of T_g illustrate the essential problem at hand.

Underlying these measurements is the assumption that methods to estimate T_g in bulk materials are equally applicable to

Significance

The disparate results for T_g shifts of polymer thin films raise the question of whether T_g provides a good metric to characterize changes in the overall dynamics of these films. Our work demonstrates how different techniques to measure T_g are influenced by the relaxation gradient across the film. We find that different measurement methods can provide contradictory T_g estimates, depending on their sensitivity to dynamics near the substrate, providing a possible explanation for prior contradictory results. We take advantage of these differences by combining T_g estimates to predict T_g near the substrate. Our findings should be useful for polymer thin film applications, including microelectronic devices, lithium battery technology, and the development of biomedical devices.

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ultrathin films. Given the presence of significant mobility gradients and conflicting T_g results, we raise the question of whether T_g alone is a useful way to characterize dynamic changes in ultrathin films. To address this question, we carried out molecular dynamics simulations of thin polymer films having variable thickness and polymer–substrate interaction strength. We use both thermodynamic and dynamic definitions of T_g to show that these different T_g metrics can give qualitatively different indications of how film confinement influences glass formation. While it is evident that the community needs more direct measures of the mobility gradient across the film, as well as direct measures of relaxation time of the film as whole, we propose an approach to combine thermodynamic and dynamic estimates of T_g to distinguish the substrate T_g from the upper layers of the film. Thus, we do not suggest that we abandon T_g as a tool to characterize thin polymer films. Instead, these measurements need to be considered in the context of which aspects of the mobility gradient they best reflect and how they can be combined to yield a more complete picture of the film dynamics.

Results and Discussion

To illustrate the nature of the conflict among various measures of T_g , we first contrast T_g of the polymer film derived from both thermodynamic and dynamic approaches in Fig. 1. For thermodynamic definitions of T_g , we examine measurements of film thickness (Fig. 1A) (analogous to ellipsometry measurements) or film potential energy (Fig. 1B) [analogous to differential scanning calorimetry (DSC) measurements]. As observed in many experiments (3, 6, 15, 21, 38–40), we find a decrease of T_g for thinner films for the entire range of polymer–substrate interaction strength ε examined—even when substrate interactions are three times larger than those of the polymer–polymer interactions. In contrast, if we use a purely dynamic definition of T_g from the incoherent intermediate scattering function, which is closely related to inelastic neutron-scattering experiments, we find that T_g decreases for small ε , but increases when substrate–polymer interaction strengths exceed those of the polymer–polymer interaction strengths, $\varepsilon \gtrsim 1.0$. Thus, when the polymer–substrate interaction strength exceeds the polymer–polymer interaction strength, the thermodynamic and dynamic definitions of T_g qualitatively disagree, the primary phenomenon that we address. We explain the technical procedure for these estimates of T_g in *SI Appendix, section II*.

Film Dynamics and Relaxation Gradient. To explain the differences in T_g values, we focus on polymer relaxation and its spatial variation. One common method to quantify the relaxation dynamics of the film is through the self-part of the intermediate scattering function,

$$F_s(q_0, t) = \frac{1}{N} \left\langle \sum_{j=1}^N \exp[i\mathbf{q} \cdot (\mathbf{r}_j(t) - \mathbf{r}_j(0))] \right\rangle, \quad [1]$$

evaluated at q_0 , corresponding to the nearest-neighbor periodicity, so that we are determining a segmental relaxation time; the subscript s in F_s stands for self. We also considered smaller q corresponding to scale of the chain radius of gyration, as well as the center of mass relaxation, and we find results very similar to those presented below (*SI Appendix, section III*). $F_s(q_0, t)$ can also be determined as a function of monomer position, which allows us to probe relaxation gradients in the film. Representative data for $F_s(q_0, t)$ for several film thicknesses and substrate interactions are shown in Fig. 2. For weak substrate–polymer interactions ($\varepsilon \leq 1.0$), we use a two-step relaxation function to describe the data in Fig. 2,

$$F_s(q_0, t) = (1 - A)e^{-(t/\tau_s)^{3/2}} + Ae^{-(t/\tau_\alpha)^\beta}, \quad [2]$$

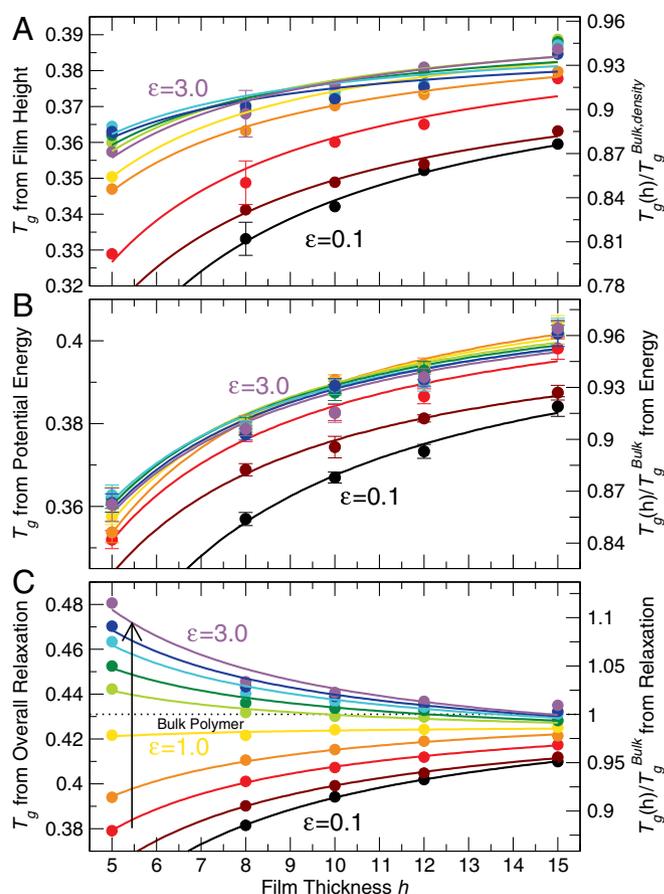


Fig. 1. (A–C) The glass transition temperatures T_g of thin polymer films, defined from the T dependence of (A) film height and (B) potential energy, and (C) a fixed relaxation time [$\tau(T_g) = 10^3$] plotted as a function of film thickness h for polymer–substrate interaction strengths $\varepsilon = 0.1, 0.25, 0.5, 0.75, 1.0, 1.25, 1.5, 2.0, 2.5,$ and 3.0 (bottom to top). On the right side of the vertical axis, we normalize each definition of T_g by the corresponding glass transition temperature of the bulk polymer T_g^{Bulk} . For A, we use T_g^{Bulk} defined by the T dependence of density on heating, the nearest equivalent to film thickness. For both A and B, we average T_g obtained from at least three independent runs and show the representative SE of the T_g estimates. For extremely thin films $h \leq 5$, polymers do not adhere to the substrate for weak substrate interactions ($\varepsilon = 0.1, 0.25$), and thus we exclude T_g values for those films. The lines are a guide for the eye and come from a fit to a model for the thickness dependence of T_g (ref. 37 and *SI Appendix, section IV*).

where τ_α is the primary or “ α -relaxation time”; the vibrational relaxation time $\tau_s \approx 0.30$ is nearly constant for all film heights h , temperatures T , and ε studied. For strong polymer–substrate interactions ($\varepsilon \gtrsim 1.0$), we follow earlier works (41–44) that examine the emergence of a bound layer near the substrate, which requires that we add an additional relaxation process to Eq. 2 to explicitly describe the bound layer relaxation time τ_b near the substrate,

$$F_s(q_0, t) = (1 - A)e^{-(t/\tau_s)^{3/2}} + (A - A_b)e^{-(t/\tau_\alpha)^\beta} + A_b e^{-(t/\tau_b)^{\beta_b}}, \quad [3]$$

where A_b/A can be associated with the fraction of the substrate bound polymer segments N_b/N ; τ_α is dominated by the relaxation of the unbound polymers in the film, and β and β_b are the stretching exponents for unbound and bound layer relaxations, respectively. We use Eq. 3 to fit $F_s(q_0, t)$ in Fig. 2. From these data, it is apparent that for a sufficiently large ε , the relaxation from the plateau region is a multistep process, due to the

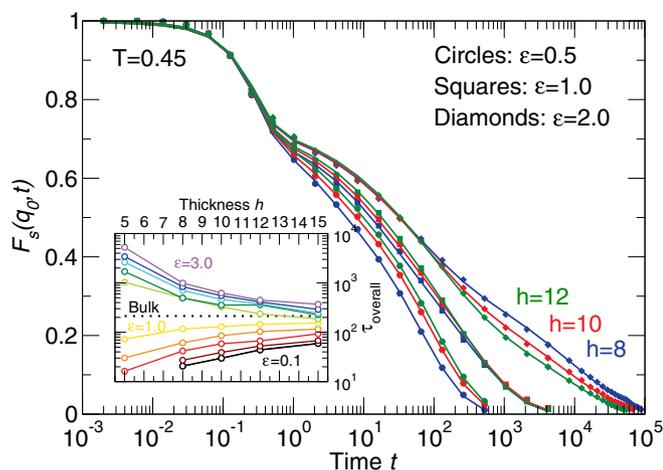


Fig. 2. The self-part of the intermediate scattering function $F_s(q_0, t)$ of thin polymer films at $T = 0.45$ for representative polymer–substrate interaction strengths, $\varepsilon = 0.1, 1.0,$ and 2.0 and for representative film thickness $h = 8, 10,$ and 12 . Symbols are simulation data and lines are fits from Eqs. 2 and 3. The maximum root-mean-square deviation of all of the fits is 6.6×10^{-3} . The black, red, and green curves represent film thickness $h = 8, 10,$ and 12 , respectively. For $\varepsilon = 2.0$, the relaxation is substantially suppressed compared with smaller ε with the same film thickness. *Inset* shows the thickness dependence of overall film relaxation time τ_{overall} . When the strength of the polymer–substrate interaction is nearly identical to the polymer–polymer interaction strength, τ_{overall} is nearly independent of film thickness.

presence of a large relaxation gradient near the interface. We address this complication below.

To understand the contradictory estimates of T_g from thermodynamic and dynamic properties when the substrate is strongly attractive (Fig. 1), we focus on the gradient of the relaxation time in the polymer film in Fig. 3. Since the ultimate goal of reporting T_g changes is to inform on the dynamics of the polymer film, we quantify the relaxation time of monomers across the film profile $\tau(z)$ by partitioning $F_s(q_0, t)$ into layers of thickness 0.875 parallel to the substrate; this layer size is similar to the spacing between monomers perpendicular to substrate direction, although the precise value of size used to group layers does not affect our findings. Monomers are associated with a layer based on their location at the time origin over which $F_s(q_0, t, z)$ is calculated, and we average over many such time origins. Note that because $F_s(q_0, t, z)$ is restricted to a local region, the gradient of mobility does not introduce a multistep decay from the plateau; in other words, the decay of $F_s(q_0, t, z)$ from the plateau can be described by a single stretched exponential function, with a corresponding relaxation time $\tau(z)$. Fig. 3 shows the relaxation time $\tau(z)$ as a function of the distance from the substrate z for several representative ε and film thicknesses h . We see that there is a significant mobility gradient across the film for all of the film thicknesses; the relaxation time near the substrate varies substantially with ε , spanning over three decades of time. Near the free surface, the relaxation time of all of the films is nearly the same for all of the thicknesses and ε studied; this result has also been observed in experiments (8, 45).

Local Dynamic T_g . We suspect the large mobility gradient in the film is the origin of differences in the T_g values reported by the thermodynamic and dynamic definitions of T_g . Thus, we examine how T_g varies in different regions of the film and how this compares to our previous T_g estimates. To evaluate a dynamic T_g for different parts of the film, we need to evaluate the T dependence of relaxation time in each part of the film. Following a commonly invoked description of polymer films, we find it instructive to group the film into three parts—(i) a free sur-

face layer, (ii) the middle layer, and (iii) the substrate layer. The free surface layer is defined by the top part of the film with a thickness of 1.75σ , corresponding to roughly two monomer “layers”; provided we average over an interfacial scale less than four monomer diameters at the free surface, the precise scale we choose is not important for the qualitative trends we report. The middle layer is defined by the central two monolayers (corresponding to a thickness 1.75σ). To ensure the robustness of our findings, we also varied the scale of the middle region from one monolayer up to four monolayers and see no qualitative changes of our results. We can quantitatively estimate the thickness of the bound substrate layer h_{sub} using our fits (Eq. 3) to $F_s(q_0, t)$. Since $A_b/A \approx N_b/N$, the fraction of substrate bound segments, the substrate layer thickness $h_{\text{sub}} \approx hA_b/A$. Clearly, this definition is valid only when there are bound segments, which occurs for $\varepsilon \gtrsim 1.0$. Fig. 3, *Inset* shows that h_{sub} approaches a constant value (≈ 4) for thick films; for $h \lesssim 10$, h_{sub} decreases due to strong finite-size effects in very thin films. We find that h_{sub} is nearly independent of temperature and ε (above the threshold for bound segments), and thus we have reported h_{sub} averaged over various ε . In the case where there is no bound substrate layer ($\varepsilon < 1.0$), we use the same values for h_{sub} shown in Fig. 3, *Inset* so that we have a comparable scale to define the substrate relaxation for all interaction strengths. Note that for $h = 5$, the film is so thin that the three regions are not readily distinguishable, so that the results for the thinnest film deviate from those for all other thicker films.

Using these definitions of film regions, we average the relaxation time in each of these three layers for all of the film thicknesses h , temperatures T , and polymer–substrate interaction strengths ε and obtain relaxation times for the interface $\tau_{\text{int}}(\varepsilon, T, h)$, middle $\tau_{\text{mid}}(\varepsilon, T, h)$, and substrate $\tau_{\text{sub}}(\varepsilon, T, h)$. Fig. 4 shows τ for these layers as a function of inverse temperature $1/T$ for representative film thicknesses h and interaction strengths ε . The relaxation time of the free surface layer τ_{int} is independent of film thickness and ε (excepting the thinnest film, $h = 5$). The relaxation time of the middle film τ_{mid} is nearly the

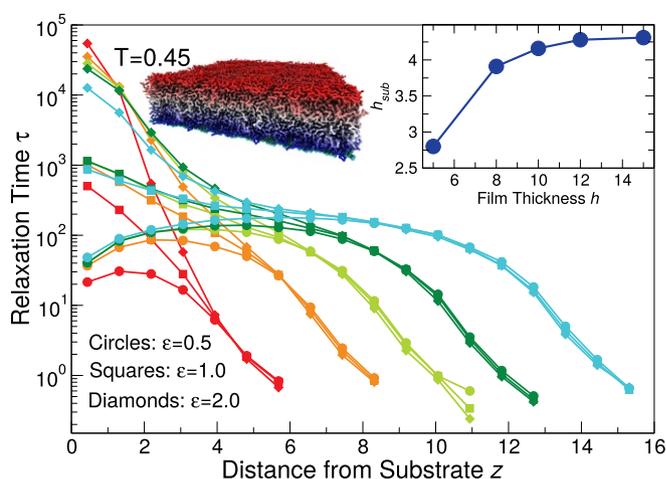


Fig. 3. The spatial variation of relaxation time $\tau(z)$ at $T = 0.45$ for various film thicknesses $h = 5$ (red), 8 (orange), 10 (light green), 12 (green), and 15 (light blue) and representative polymer–substrate interaction strength $\varepsilon = 0.5$ (circles), 1.0 (squares), and 2.0 (diamonds). The relaxation time near the substrate spans over three decades of time for the range of ε shown here. The picture shows an illustration of the mobility gradient of the thin polymer film with a strongly interacting substrate; colors indicate the logarithmic scaled relaxation time from red (most mobile) to blue (least mobile). *Inset* shows the bound layer thickness h_{sub} as a function of the overall film thickness; h_{sub} is nearly T and ε independent, and so we show an average over strong substrate interaction strengths $\varepsilon \gtrsim 1.25$.

substrate effects can be masked by a nearly immobile polymer layer at the substrate when ε is large; this is the so-called “cloaking” effect with strong substrate interactions. In contrast, the relaxation time of the film as a whole averages over the entire mobility gradient, which incorporates the effects of a slow substrate layer at strong interaction strength. It is for this reason that the thermodynamic and dynamic definitions can qualitatively differ for large substrate attraction strength. Consequently, the differences in T_g from the thermodynamic and dynamic approaches are not contradictory; rather, they inform on different aspects of the film dynamics. The difference in sensitivity of thermodynamic and dynamic T_g measurements is consistent with that obtained in recent simulations of free-standing films (46). From a more general perspective, the combination of these measurements could be helpful to estimate mobility gradients in thin films that are otherwise difficult to measure experimentally.

To build on this idea, we develop a simple model that allows us to estimate T_g of the substrate layer using only T_g data for the overall film that are readily accessible to experiments. To do so, we consider that our data suggest that the dynamic T_g is a combination of the T_g of bound substrate layer and unbound layers of the film, weighted in proportion to their respective thicknesses. Since we have shown that the thermodynamic estimate of T_g appears to report only on the “unbound” portions of the film, we can write a simple superposition description that allows us to predict T_g^{sub} , as,

$$\tilde{T}_g^{\text{sub,dyn}}(h) = \frac{h}{h_{\text{sub}}} \tilde{T}_g^{\text{dyn}}(h) - \frac{h - h_{\text{sub}}}{h_{\text{sub}}} \tilde{T}_g^{\text{thermo}}(h), \quad [4]$$

where \tilde{T}_g is the glass transition temperature relative to the bulk value for the specific measurement method; this relative value accounts for minor differences in T_g of the bulk material based on the technique used. This model applies only to cases where there is a distinct bound layer that the thermodynamic definition is not sensitive to (here, $\varepsilon > 1.0$). The substrate layer thickness h_{sub} is determined from the relaxation of $F_s(q_0, t)$, as shown previously in Fig. 3, *Inset*. We test our prediction for T_g^{sub} using as an input our measured dynamic and thermodynamic T_g values and comparing them to the T_g^{sub} value directly evaluated from

the relaxation time of the substrate layer. Fig. 6 shows the actual (solid circles) and predicted (solid curves) T_g^{sub} values from Eq. 4, which demonstrates that the simple layer model can reasonably predict the substrate relaxation. Since thermodynamic and dynamic T_g measurements are experimentally possible, this model provides a way to experimentally estimate the substrate layer T_g for strongly attractive substrates, without needing to directly probe substrate dynamics.

Conclusions

We used molecular dynamics simulations to study the origin of the T_g shifts in supported coarse-grained polymer films with variable film thickness and polymer–substrate interaction strength, ε . In particular, we investigated the impact of the mobility gradient within the thin polymer film on widely used methods for defining T_g of these films. When the polymer–substrate interaction strength is less than that of the polymer–polymer interaction strength ($\varepsilon \lesssim 1.0$), thermodynamic definitions of T_g from film thickness and enthalpy, as well as a dynamic definition of T_g from the density–density correlation function, all show a decreasing T_g with decreasing film thickness, as anticipated by many previous experimental studies (3–10, 12–15). When the substrate interaction strength is greater than polymer–polymer interaction strength, the thickness dependence of the thermodynamic and dynamic measurements of T_g decouples; specifically, T_g from thermodynamic approaches still decreases with decreasing film thickness, while the dynamic T_g increases with decreasing thickness. Apparently, on decreasing film thickness, T_g estimated from the thermodynamic approaches is more strongly affected by the growing proportion of the free interfacial layer than by the substrate layer. This observation is consistent with the behavior of polymer–nanoparticle composites with strong polymer–nanoparticle interactions (41, 47–50). On the other hand, the slow relaxation near an attractive substrate significantly contributes to the dynamically determined relaxation of the film as a whole, so that the dynamically defined T_g increases for large ε . The differences in sensitivity of these approaches to the relaxation near the film substrate lead to a decoupling between the thermodynamically and dynamically defined T_g when substrate interactions are strong. Of course, we must be cautious about the generality of these findings since there are also experimental reports of increases of T_g from thermodynamic methods (11, 18, 19, 51). Our important take-home message is that the different measurement methods can indeed yield qualitatively different estimates of T_g .

The disparate results for T_g raise the question of whether any single method provides a good metric for characterizing the dynamics of ultrathin polymer films. We propose that the answer to this question is “no.” Since the dynamics of these films differ substantially from the free surface to the substrate layer, attempts to characterize the dynamic changes in terms of changes in a single variable are inadequate. This is especially true in the case of a supported film on a strongly interacting substrate, where the dynamics at the substrate and free interface exhibit opposite changes relative to the bulk material. At best, changes in the value of T_g report on some average of this gradient in mobility. On the other hand, these measurements are still valuable. Our results suggest that T_g estimates from different approaches are sensitive to the different regions within the film. Thus, a combination of such measurements can be informative on the more detailed picture of the gradient in molecular mobility of the film. Indeed, we developed a simple approach that suggests we can predict T_g near the substrate of a film using only data for the mean T_g obtained from thermodynamic and dynamic methods. It will be valuable to test this approach experimentally. However, careful measurements of the gradient of relaxation across the film profile are ultimately needed to provide a complete picture of the film dynamics.

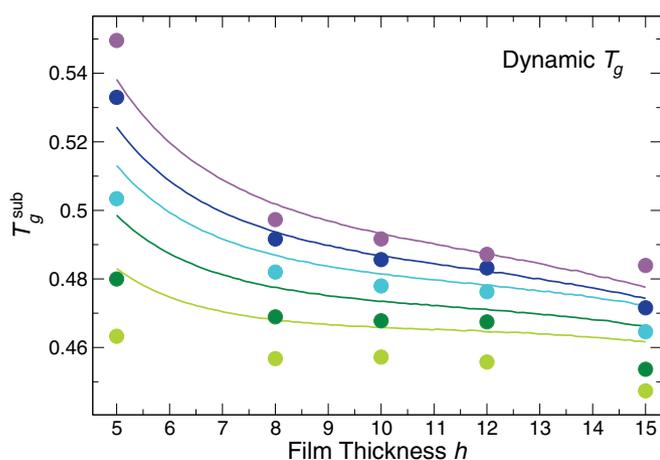


Fig. 6. Comparison of the predicted dynamic substrate glass transition temperatures T_g with values obtained from simulation. The solid circles are the T_g^{sub} values directly obtained from our data (same data as in Fig. 5A) with $\varepsilon = 1.25, 1.5, 2.0, 2.5,$ and 3.0 . The solid curves are the T_g^{sub} values predicted from Eq. 4. The curves are obtained by first fitting the thickness dependence of the mean $T_g(h)$ values from dynamic and thermodynamic methods using a Gibbs–Thomson-inspired model (see *SI Appendix, section IV* for a description).

Simulation Methods

We simulate supported thin polymer films with variable film thickness h and strength of attractive interaction ε between the substrate and polymer, using molecular dynamics simulations. The polymer film model is the same as that used in refs. 37 and 44. The polymer films have 200, 320, 400, 480, or 600 polymer chains; these films have thicknesses $h \approx 5\sigma, 8\sigma, 10\sigma, 12\sigma,$ and 15σ , respectively, which decrease approaching T_g . These films are referred to as $h = 5, 8, 10, 12,$ and 15 . Above the film is free (empty) space, so the film is effectively at pressure $P = 0$.

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