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Effects of a "bound" substrate layer on the dynamics of supported polymer films

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It is widely appreciated that an attractive polymer-substrate interaction can slow relaxation in thin supported polymer films and polymer nanocomposites. Recent measurements and simulations on nanocomposites have indicated that this slowing of polymer dynamics occurs more strongly near a highly attractive particle surface where a "bound" layer having a much lower mobility can form, strongly influencing the thermodynamics and dynamics of the film. Here we use molecular simulations to show that a bound interfacial layer having a very similar nature arises in thin supported polymer films when the polymer-polymer attraction is stronger than the polymer-polymer interaction strength. This bound polymer layer effectively insulates the remainder of the film from the strong interfacial interactions, and the resulting thermodynamically determined T_g is relatively insensitive to the polymer-substrate interaction strength when it exceeds that of the polymer-polymer interactions. The presence of this layer gives rise to an additional relaxation process in the self-intermediate scattering function that is not observed in the bulk material and leads to a slowing down of the average relaxation time of the film as a whole. On the other hand, the average relaxation time of the film outside the bound layer does not grow in proportion to the strength of the substrate attraction due to the weak coupling of the substrate relaxation to the relaxation in the interior of the film. At large substrate attraction, the bound layer effectively "cloaks" the substrate, reducing the effect of the polymer-surface interaction on T_g. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4994064]

I. INTRODUCTION

Confinement of polymers is well known to substantially alter thermodynamics and dynamics of glass-forming materials.[1] Since the pioneering work of Keddie and Jones in 1994,[2] thin polymer films have received attention, and a large body of research has verified that the glass transition of spin-coated thin polymer films can be substantially altered from the bulk material.[3–9] A general consensus has emerged that there are significant mobility gradients in these films near the polymer-substrate and polymer-air interfaces. In supported films, the free surface has enhanced dynamics relative to the interior of the film, which tends to decrease the overall T_g of polymer films.[10,11] In contrast, the dynamics of the polymer material near an attractive supporting substrate is typically slower relative to the film interior, an effect that can negate the opposite effect of the polymer-air boundary to give rise to an increase in T_g if the attractive interaction is sufficiently strong.[1,6–8,12–21] That said, a weakly attractive substrate can exhibit enhanced substrate dynamics.[22] The overall change in T_g for a supported film then results from the competition between these interfacial effects, as well as effects due to the intrinsic geometrical confinement. Although it is challenging to separate the role played by each of these effects, recent studies have indicated that the changes in the dynamics of glass formation can be understood in terms of how collective motion and the enthalpy and entropy of activation for segmental motion become altered in thin polymer films.[23,24]

The simplistic view that T_g changes simply reflect the substrate interaction strength can be countered by observations indicating that this trend does not always apply. Some measurements have indicated little or no change in the thermodynamically estimated T_g, even when the polymer-substrate interaction is highly attractive.[25–29] Similarly, polymer-nanoparticle composites have also been observed to exhibit little change in the thermodynamic estimates of T_g in comparison to the bulk material for strongly interacting nanoparticles,[30–33] and the dynamics of nanocomposites have been shown to be closely analogous to thin polymer films.[7,34] A recent computational study suggests that the lack of sensitivity of the thermodynamic T_g to variation of the polymer-particle interaction is a result of the emergence of a "bound" layer of polymer in the interfacial region of the nanoparticles that "cloaks" the matrix polymers from the interfacial interactions.[35] Since it is quite plausible that a similar mechanism is at work in thin polymer films with strong substrate interactions, we investigate this possibility in the present work.

We use molecular simulations to examine the effects of substrate interaction strength on the glass transition and dynamics of simulated supported polymer films and determine if a "bound" layer near the substrate influences observed T_g changes. Similar to the case of polymer composites, we find that T_g, defined from the temperature dependence of thermodynamic properties, is nearly invariant for polymer-substrate interaction strengths greater than that of the polymer-polymer interaction. To explain the dynamical origin of this saturation

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effect, we examine the segmental dynamics near the solid substrate. We observe the formation of a bound layer when the polymer-substrate interactions exceed the polymer-polymer interaction strength. The emergence of this layer is characterized by a distinct relaxation process in the intermediate scattering function. This kinetically defined bound layer has a segmental relaxation time that can be orders of magnitude slower than that of the remaining "unbound" portion of the film. The existence of this "bound" or "dead" layer naturally explains the effective cloaking of the solid substrate such that the relaxation time of the majority of the film and the thermodynamic T_g are not greatly increased by further increases of the polymer-substrate interaction strength. In particular, T_g of the film outside the bound layer, as defined from a large fixed relaxation time, is only weakly dependent on substrate interactions when a bound layer is present, similar to the thermodynamic T_g definition. Apparently, the thermodynamic definition of T_g is dominated by the behavior of the chains that are not bound to the substrate. These results closely mirror those reported for simulations on polymer-nanoparticle composites based on the same coarse-grained polymer model as the present paper.[35]

II. MODELING AND SIMULATION DETAILS

Our findings are based on molecular dynamics simulations of a supported polymer film with various strength of attractive interaction between the substrate and polymer film. The upper interface of the film is free. The model is the same as that used for the extensive studies in Ref. 23. We model polymers as unentangled chains of 10 beads linked by harmonic springs. The harmonic spring potential $U_{\text{bond}} = \frac{k_{\text{chain}}}{2}(r - r_0)^2$ connects the nearest-neighbor within a polymer chain with an equilibrium bond length $r_0 = 0.9$ and a spring constant $k_{\text{chain}} = 1111$;[23] these values are similar to those in Ref. 36, except that r_0 is smaller to inhibit crystallization of the film. In addition, there are Lennard-Jones (LJ) interactions between unbound monomers, which are truncated at pair separations greater than 2.5σ, where σ is the monomer diameter in the LJ potential.

The substrate is modeled as a collection of 528 particles arranged in a triangular lattice [the (111) face of an FCC lattice]; particles are tethered via a harmonic potential $V_{\text{sub}}(r) = (k/2)\ (r - r_0)^2$, where r_0 is the ideal lattice position and $k = 50$ is the spring constant.[18,37] There are also LJ interactions between monomer pairs as well as between substrate and chain monomers. These interactions are truncated at $2.5\sigma_{ij}$; the subscript ij indicates the possible combinations of interactions (ss substrate-substrate, ps polymer-substrate, pp polymer-polymer). The LJ parameters are $\sigma_{pp} = 1.0$, $\varepsilon \equiv \varepsilon_{pp} = 1.0$, $\sigma \equiv \sigma_{ps} = 1.0$, $\sigma_{ss} = 0.8$, and $\varepsilon_{ss} = 1.0$, and we consider interaction strengths between monomers and substrate particles ε_{ps} = 0.1, 0.25, 0.5, 0.75, 1.0, 1.25, 1.5, 2.0, 2.5, and 3.0. Since we vary only ε_{ps} in the manuscript, we will simply refer to this value as ε for simplicity. We did not make the common assumption that the interaction strength of the monomers with the substrate follows the Lorentz-Berthelot mixing rule because we wish to examine how the strength of the polymer-substrate interaction affects the thin film dynamics without altering the internal substrate interactions.

The supported polymer films consist of 600 polymer chains of 10 beads each. We employ periodic boundary conditions in the directions parallel to the substrate with a box length of 19.76 (determined by the lattice spacing of the triangular lattice substrate), resulting in a film that is ≈15 monomers thick. The free interface of the polymer film results in a film effectively at pressure $P = 0$. We also simulate a bulk polymer with periodic boundary conditions in all directions at pressure $P = 0$ as a reference for the thermodynamic and dynamic polymer properties. All simulations are performed using LAMMPS.[38] Simulations are performed in an NVT ensemble via the Nose-Hoover algorithm with time step 0.002, excepting cooling and heating runs of the bulk polymer, which are run in an NPT ensemble at $P = 0$. We perform at least 5 independent heating and cooling runs for the both the pure polymer and polymer film at the same rate 10^{-5}. Trajectories at fixed temperature to evaluate dynamical properties are generated from configurations taken from the heating run to perform simulations under isothermal-isobaric conditions for the pure polymer with pressure $P = 0$; NVT ensembles with a fixed box size are used for the supported polymer film. We vary the temperature from 0.45 to 0.65, above (the heating rate dependent) $T_g \approx 0.40$ of the polymer film. Each trajectory is equilibrated for at least 100 times the overall polymer relaxation time τ. Our reduced units can be mapped into physical units relevant to the common polymer materials, such as polystyrene with $\sigma \approx 1$ nm, 1 time unit ≈1 ps, $\varepsilon \approx 1$ kJ/mol, and $T_g \approx 100\,^{\circ}$C.

III. RESULTS AND DISCUSSION

We first examine the effect of the polymer-substrate interaction strength ε on the glass transition temperature T_g of the polymer film, as defined by the variation of thermodynamic variables with temperature. In general, the precise value for the glass transition temperature T_g obtained from the thermodynamic approach depends both on the quantity examined and the feature used to define T_g. Accordingly, we consider several possible definitions of T_g to ensure that our qualitative findings are not sensitive to the choice. Experimentally, measurements of the specific heat using differential scanning calorimetry (DSC), or the film thickness using ellipsometry, are rather standard methods for estimating T_g, and we first consider these metrics.

To determine results comparable to a DSC measurement from our simulations, we evaluate the temperature dependence of the energy $U(T)$ during heating the glassy film, equivalent to the integrated specific heat (in the supplementary material, we directly examine specific heat). To compare with trends from ellipsometry measurements, we evaluate the temperature dependence of the film thickness $h(T)$ during heating. We obtain $U(T)$ and $h(T)$ from heating the supported polymer film at a fixed rate 10^{-5} from $T \approx 0$ for all ε studied. Deep in the glass regime ($T < 0.25$), U_{glass} and h_{glass} can both be well-described by quadratic functions (see supplementary material for a detailed discussion of the fitting of the data to empirical functions); quadratic behavior of U_{glass} corresponds to commonly observed linear temperature dependence of the specific heat in the glass state. To eliminate this trivial dependence of energy and thickness on temperature in the glass, we focus on the T dependence of excess potential energy relative to the glass,

$$\Delta U(T) = U(T) - U_{\mathrm{glass}}(T), \tag{1}$$

shown in Fig. 1, and excess film height relative to the glass,

$$\Delta h(T) = h(T) - h_{\mathrm{glass}}(T), \tag{2}$$

shown in Fig. 2. We define T_g as the vanishing temperature $\Delta U(T_g) \to 0$ or $\Delta h(T_g) \to 0$ from a linear extrapolation of the T dependence of $\Delta U(T)$ and $\Delta h(T)$ in the fluid state, as indicated by the fits in Figs. 1 and 2. In both cases, we find that T_g increases with ε up to ≈1.25, a strength similar to the polymer-polymer interaction; T_g plateaus for larger ε. That said, the precise value of T_g, and the degree of variation with ε depends on the specific film property considered. Not surprisingly, T_g from the film height is lower than that of the energy since the highly mobile free interface layer plays a larger role in height than the overall energy. A similar saturation of T_g is reported by Xia *et al.*[39] although the amplitude of the polymer-substrate interaction relative to the polymer-polymer interaction is substantially larger than that considered here. The same saturation behavior has also been reported in simulation of polymer-nanoparticle composites.[35]

To reaffirm that the variation of T_g is not sensitive to the specific thermodynamic quantity and feature specified [e.g., $\Delta U(T_g) \to 0$], we have also examined excess specific heat, and consider T_g defined by a total of five different possible features in the T-dependence. As shown in the supplementary material, we confirm that the variations of the polymer film T_g with respect to ε exhibits that same qualitative behavior, independent of the definition chosen, providing some assurance in the robustness of these findings.

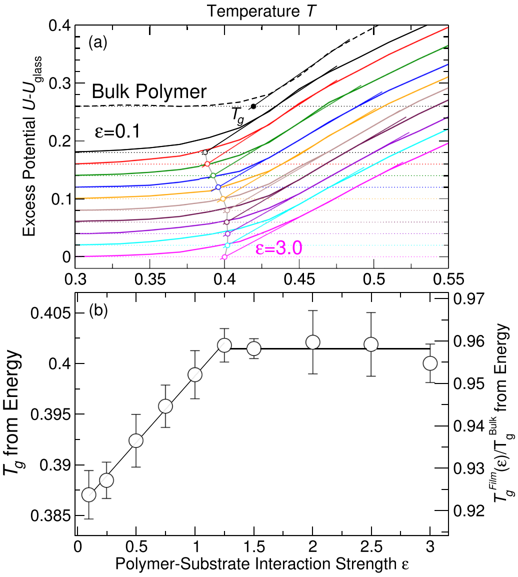

FIG. 1. (a) The excess potential energy $\Delta U(T) = U(T) - U_{\mathrm{glass}}(T)$ for many values of the polymer-substrate interaction strength ε. For each ε, the potential energy is averaged over 5 independent runs. T_g is defined by the vanishing temperature $\Delta U(T_g) \to 0$ from a linear extrapolation of $\Delta U(T)$ above the transition region. The circles are the resulting T_g for each ε. The black dashed line is the excess potential energy of the bulk polymer. Curves are shifted vertically for clarity. From top to bottom, curves represent polymer-substrate interaction strength $\varepsilon = 0.1$, 0.25, 0.5, 0.75, 1.0, 1.25, 1.5, 2.0, 2.5, and 3.0. (b) T_g as a function of ε determined from panel (a). T_g saturates to a nearly constant value for large ε. The error bars indicate the standard error of the mean of the T_g fluctuations among 5 independent runs. On the right side of the panel, we normalize $T_g^{\mathrm{film}}(\varepsilon)$ from potential energy by the corresponding T_g from the bulk polymer.

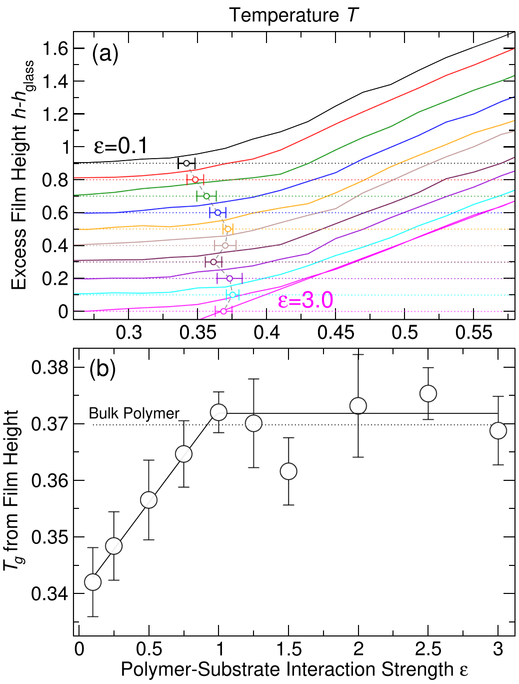

FIG. 2. (a) The excess film height $\Delta h(T) = h(T) - h_{\mathrm{glass}}(T)$ for many values of the polymer-substrate interaction strength ε. For each ε, the film height is averaged over 15 independent runs. T_g is defined by the vanishing temperature $\Delta h(T_g) \to 0$ from a linear extrapolation of $\Delta h(T)$ above the transition region. The circles are the resulting T_g for each ε. Curves are shifted vertically for clarity. From top to bottom, curves represent polymer-substrate interaction strength $\varepsilon = 0.1$, 0.25, 0.5, 0.75, 1.0, 1.25, 1.5, 2.0, 2.5, and 3.0. (b) The resulting T_g as a function of ε, from the data in panel (a), is nearly invariant at large ε. The black dashed line indicates the T_g of bulk polymer, defined by the T-dependence of density during heating. The error bars indicate the standard error of the mean of T_g estimates from 15 independent runs.

Having shown that the variation of T_g is not strongly dependent on the polymer-substrate interaction for $\varepsilon \gtrsim 1.25$ from thermodynamic quantities, a natural question to ask is: how do the dynamics of the film vary with the polymer-substrate interaction? Therefore, we start by examining the structural relaxation of the polymer film and its spatial variation across the film profile via the self-part of the intermediate scattering function,

$$F_s(q,t) = \frac{1}{N}\left\langle \sum_{j=1}^{N} \exp[i\boldsymbol{q}\cdot(\boldsymbol{r}_j(t)-\boldsymbol{r}_j(0))]\right\rangle, \tag{3}$$

evaluated at q_0, corresponding to the nearest neighbor periodicity. To quantify the spatial variation of relaxation, we partition $F_s(q, t)$ into layers of thickness 0.875, where the monomers are split among layers based on their location at the time origin $t = 0$, and average over many such time origins. Figure 3 shows $F_s(q, t)$ as a function of position in the film for fixed $T = 0.45$ for sample weak ($\varepsilon = 0.1$) and strong ($\varepsilon = 2.0$) substrate interactions. As expected, $F_s(q, t)$ exhibits a significantly suppressed polymer relaxation time near the substrate with a strong polymer-substrate interaction and a significantly

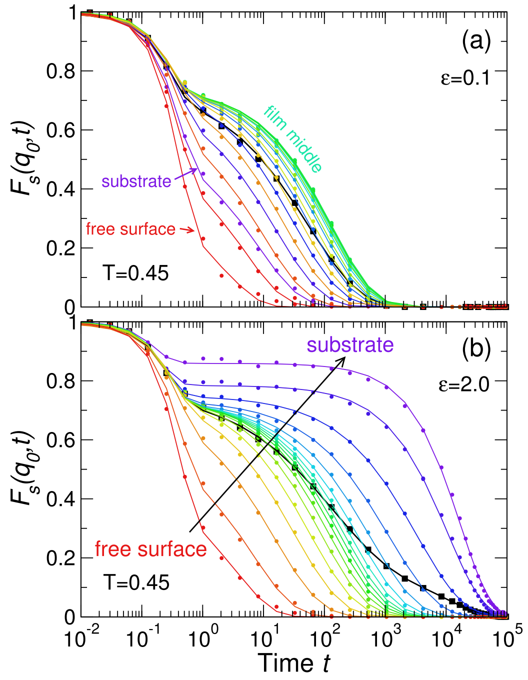

FIG. 3. The self-intermediate scattering function $F_s(q_0, t)$ at $T = 0.45$ for representative polymer-substrate interaction strengths (a) $\varepsilon = 0.1$ and (b) $\varepsilon = 2.0$. Symbols are simulation data and lines are the fit defined by Eq. (4). The thick black curves and symbols are $F_s(q_0, t)$ for the film as a whole; each colored curve represents a layer of polymer of thickness $\delta = 0.875$ parallel to the substrate; curves are color-coded from purple (near substrate), green (middle of the film) to red (free surface). For $\varepsilon = 2.0$, the relaxation near the substrate is suppressed significantly compared to the overall dynamics, while for $\varepsilon = 0.1$, the substrate interface relaxation is enhanced.

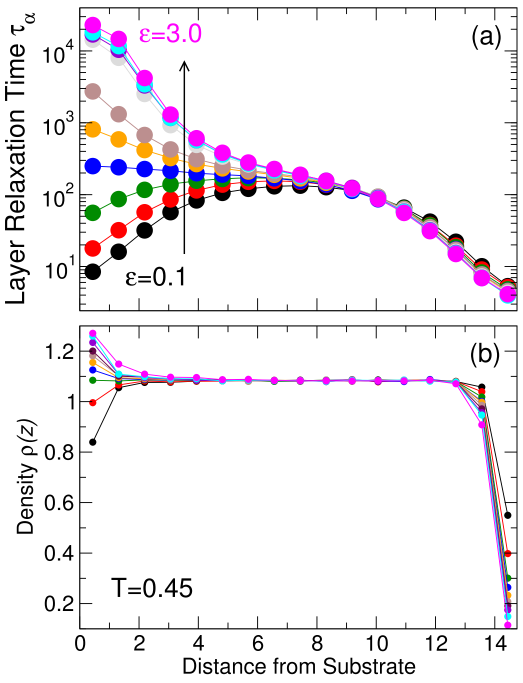

FIG. 4. (a) The spatial variation of the relaxation time $\tau(z)$ at a representative temperature $T = 0.45$ for polymer-substrate interaction strengths $\varepsilon = 0.1$, 0.25, 0.5, 0.75, 1.0, 1.25, 1.5, 2.0, 2.5, and 3.0 (from bottom to top). A crossover polymer-substrate interaction strength occurs near $\varepsilon_c \approx 0.75$, where the substrate neither suppresses nor enhances monomer relaxation near the substrate, relative to the relaxation in the middle of the film. The symbols represent the relaxation time obtained from Eq. (4). (b) The monomer density profile of the films for the same ε showed in panel (a). Unlike the relaxation time, the substrate interactions only affect the density very near to the substrate.

enhanced relaxation with a weak polymer-substrate interaction. The polymer relaxation in each layer can be described by a two-step process,

$$F_{\mathrm{self}}(q_0,t) = (1-A)e^{-(t/\tau_s)^{3/2}} + Ae^{-(t/\tau_\alpha)^{\beta}}, \qquad (4)$$

where the short-time vibrational relaxation time $\tau_s \approx 0.30$ is nearly constant for all temperatures and ε studied; the $t^{3/2}$ dependence of the mean square segmental displacement, along with the essentially Gaussian distribution of molecular displacements at short times, is consistent with a "fast" dynamics described by fractional Brownian motion.[40]

To better illustrate the variations of monomer relaxation near the substrate, Fig. 4(a) shows the characteristic relaxation time $\tau(z)$ for many ε, where z is the distance from the substrate. We see that the relaxation time τ of the layer closest to the substrate changes substantially with ε, spanning over 4 decades. For $\varepsilon \approx 0.75$, the relaxation near the substrate is neither enhanced nor suppressed; instead, it is nearly a continuation of the relaxation in the middle of the film, similar to prior observations.[23,35] Such a crossover, similar to a critical unbinding condition ε_c, indicates a balance between the favorable polymer-substrate interaction and the geometric confinement limiting the number of polymer configurations available near the substrate. For the strong polymer-substrate interaction strength, the relaxation is significantly reduced compared to the middle region of the film, approaching the limiting case of an irreversibly adsorbed layer near the substrate, as observed in the experiments.[25,41] For comparison, we also show the monomer density profile of the films in Fig. 4(b). Near the substrate, the monomer density increases with increasing ε, but the changes to the density profile are not nearly so pronounced as those of the relaxation. Thus, as expected from an earlier work,[42] the density is not the sole factor controlling changes in the film dynamics.

Such spatially resolved relaxation is not readily accessible experimentally. Consequently, we next show how these interfacial differences affect the overall film relaxation. Figure 5(a) shows the overall $F_s(q_0, t)$ for $0.1 \le \varepsilon \le 3.0$ at a representative temperature $T = 0.45$. For $\varepsilon \ge 1.0$, we can identify a distinct relaxation process in the time scale beyond the α-relaxation time. This relaxation process apparently emerges from a bound layer near the substrate due to the strong polymer-substrate interactions, analogous to the "bound polymer" in the interfacial region of a nanoparticle with strong polymer-nanoparticle interactions. As a consequence, the overall $F_s(q_0, t)$ cannot be described by Eq. (4) for $\varepsilon \gtrsim 1.0$. Following earlier studies,[35,43,44] we add an additional relaxation process to Eq. (4) to explicitly describe the bound layer relaxation time τ_b,

$$F_s(q_0,t) = (1-A)e^{-(t/\tau_s)^{3/2}} + (A-A_b)e^{-(t/\tau_\alpha)^{\beta}} + A_b e^{-(t/\tau_b)^{\beta_b}}, \qquad (5)$$

where A_b can be associated with the fraction of the substrate bound polymers 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. Figure 5 shows the resulting fits from Eq. (5) (solid lines), which describe well the relaxation of the film with a bound polymer layer for $\varepsilon > 1.0$. We emphasize that, for the

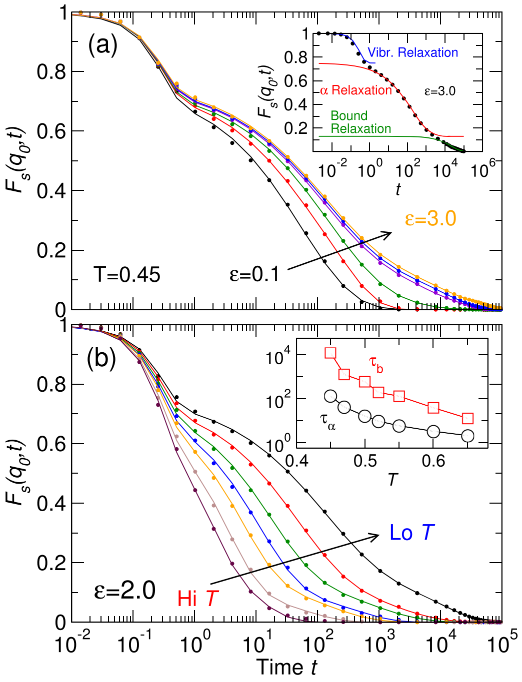

FIG. 5. (a) The self-intermediate scattering function $F_s(q_0, t)$ at a representative temperature $T = 0.45$ for polymer-substrate interaction strengths $\varepsilon = 0.1$, 0.75, 1.25, 1.5, 2.0, and 3.0 (from left to right). For clarity, not all interaction strengths are shown in the figure. For $\varepsilon \geq 1.5$, an additional relaxation emerges at large time scales, corresponding to the relaxation of the "bound" substrate polymer layer. The solid symbols are simulation data and lines are fits obtained from Eq. (5). The inset shows how each term of Eq. (5) contributes to the overall relaxation. For clarity, the α and vibrational relaxation terms in Eq. (5) are shifted upward by A_b and $A_b + A$, respectively. (b) $F_s(q_0, t)$ for a fixed polymer-substrate interaction strength $\varepsilon = 2.0$ at $T = 0.45$, 0.47, 0.50, 0.52, 0.55, 0.60, and 0.65 (from right to left). The contribution of the bound layer to $F_s(q_0, t)$ is evidently more appreciable at low T. The inset shows the relaxation time τ_b of bound layer and the primary relaxation τ_α due to the unbound polymer as a function of T.

fits using Eq. (5), the monomers do not need to be sorted into groups; rather, since the fit to Eq. (5) is performed on the relaxation data averaged over the entire film, akin to what would be experimentally available. The non-ergodicity parameter $A \approx 0.75$ has a weak dependence on ε and T (shown in supplementary material). For $\varepsilon \leq 1.0$, the bound layer no longer exists, and so $A_b = 0$. At larger polymer-substrate interaction $\varepsilon \geq 1.5$ [Fig. 5(a)], the bound fraction A_b increases weakly from 0.10 to 0.14, corresponding to an approximate substrate interfacial scale $\xi \approx NA_b/(\rho L^2) \approx 2\sigma$. A similar value can be obtained from the distance dependence of the relaxation time $\tau(z)$ in Fig. 4. Note that, as shown in the supplementary material, the scale of the interfacial region where $\tau(z)$ deviates from the value near the film center is nearly identical for chain length 20 (twice the length discussed here); this suggests that the interfacial scale does not vary with chain length for unentangled chains. It is natural that the chain length does not play a significant role since the dynamical changes arise from changes to the local segmental dynamics, and thus a similar scale is anticipated for small molecule films. Similarly, experiments[29,45] report little to no chain length effect (even above the entanglement molecular weight). In contrast, computational studies[43,44] attribute the extra decay of the intermediate scattering function to a scale related to the chain R_g and to a polymer adsorption process, suggesting that the adsorbed layer should grow with molecular mass. The interfacial layer that we observe has no detectable mass dependence.

The T dependence of the overall relaxation function $F_s(q_0, t)$ for fixed ε [Fig. 5(b)] shows the time scale of the bound layer relaxation grows on cooling. We explicitly show the temperature dependence of the bound layer relaxation for $\varepsilon = 2.0$ in Fig. 5(b) inset. The bound layer relaxation time τ_b is about one to two decades larger than the primary film relaxation τ_α [Fig. 6(a)], consistent with the changes observed in the bound polymer layer in polymer nanocomposite experiments.[46,47] Furthermore, the bound fraction A_b also increases on cooling from 0.01 to 0.14 [Fig. 5(b)]. As an alternate representation, in Fig. 6(a), we show the dependence of the primary film relaxation (τ_α) and the bound polymer relaxation (τ_b) on ε. The substantial difference in bound (τ_b) and film relaxation (τ_α) causes the variation of overall film relaxation τ, a combination of these relaxations defined by $F_s(q_0, \tau) = A/e \approx 0.28$ to deviate from τ_α for $\varepsilon > 1.0$ (Fig. 7). Interestingly, the unbound film relaxation τ_α is nearly independent of substrate interaction for $\varepsilon > 1.0$ [Figs. 6(a) and 7], indicating that the substrate interactions have a saturating effect on the rate of relaxation near the middle of the film. This further suggests that T_g estimated from the "active material" outside the substrate interfacial region should be nearly constant for $\varepsilon > 1.0$, a point that we examine later. In Fig. 6(b), we show the stretching exponent β for the α-relaxation [Eq. (5)] is also nearly independent of substrate interaction for $\varepsilon \gtrsim 1.0$, consistent

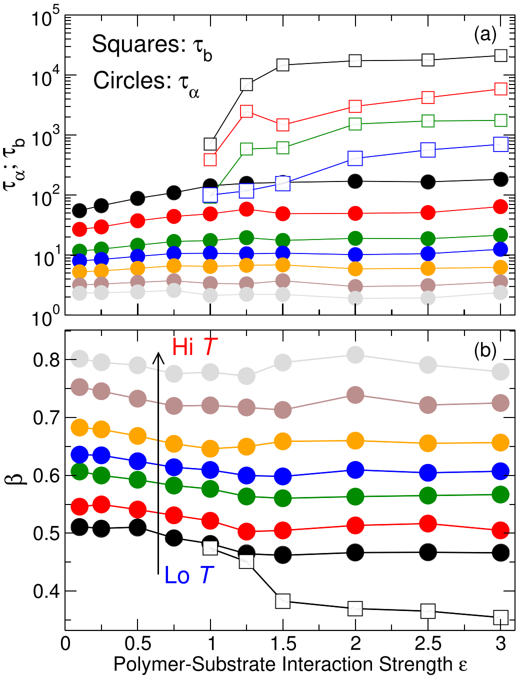

FIG. 6. (a) The relaxation time of unbound film τ_α and bound layer τ_b. From top to bottom, the temperatures are 0.45 (black), 0.47 (red), 0.50 (green), 0.52 (blue), 0.55 (yellow), 0.60 (brown), and 0.65 (grey). For $\varepsilon \gtrsim 1$ and $T \lesssim 0.52$ we can distinguish the bound relaxation, where τ_b is roughly two orders of magnitude larger than τ_α. (b) The value of the exponent β for the stretched-exponential fit of the α-relaxation in Eq. (5) (circles); β is only weakly dependent on ε. The squares show the results of fitting the relaxation without an additional bound layer [Eq. (4)], which indicates that the bound layer has the effect of decreasing the fit value of β if it is not accounted for. Such a decrease of β may provide a useful indicator that an additional process to describe relaxation data is necessary.

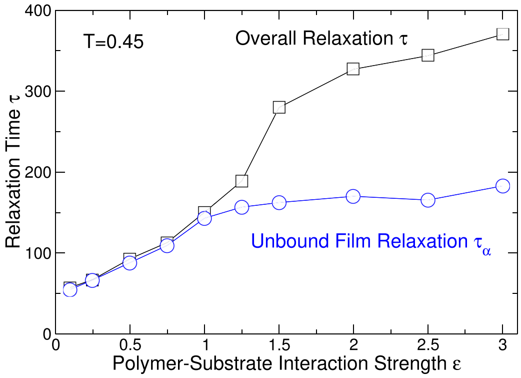

FIG. 7. The variation of the overall film relaxation τ and unbound film relaxation τ_α with respect to the polymer-substrate interaction strength ε at $T = 0.45$. For $\varepsilon \geq 1.0$, the formation of bound layer near the substrate increases the overall film relaxation, but relaxation in the unbound film is nearly independent of the substrate interaction for $\varepsilon \gtrsim 1.25$.

with the ε dependence of τ_α in Fig. 6(a). If we omit the additional bound relaxation process when we fit $F_s(q_0, t)$, there is a significant effect on the apparent value of β, which can be used as a possible indicator that an additional relaxation process is needed to describe the data. To illustrate this phenomenon, we use the two-step relaxation [Eq. (4)] to fit $F_s(q_0, t)$ of the polymer film for $\varepsilon \geq 1.0$ at the lowest T. The resulting β in Fig. 6(b) (hollow squares) shows that it is smaller than β value from a three-step relaxation, resulting from the significant gradient in the relaxation. For fixed substrate interaction strength ε, β decreases on cooling, as expected from many bulk studies.

We next examine how the bound layer affects the glass transition temperature T_g based on a dynamic definition, and how this estimate compares to T_g determined from a thermodynamic definition. To define T_g from the relaxation, we consider a parallel to the experimental convention of using a fixed relaxation time. Specifically, we chose $\tau(T_g) = 10^3$ (in LJ units); note that this fixed time scale is substantially smaller than that chosen experimentally, an inherent constraint of molecular dynamics simulations. Figure 8(b) shows T_g for the film as a whole (obtained from $\tau = 10^3$) as well as T_g for the unbound chains (from $\tau_\alpha = 10^3$). We contrast the effect of ε on the thermodynamic and dynamic definitions of T_g in Fig. 8. T_g from the potential energy and film height [Figs. 8(a) and 8(b)] increases linearly with ε up to ≈1.25–1.5 and plateaus thereafter. A similar trend is observed in the dynamic definition of T_g in the unbound portion of the film, shown in Fig. 8(c). The independence of T_g from the unbound τ_α on interaction strength is consistent with the dielectric measurements.[25,48–50] These results imply that the thermodynamic definition of T_g is insensitive to the slow relaxation of the bound layer for $\varepsilon \gtrsim 1.25$ and it directly tracks the relaxation in the unbound portion of the film. This unexpected behavior of T_g for $\varepsilon \gtrsim 1.0$ indicates that the bound polymer layer "cloaks" the strongly interacting substrate. In this context, the term "cloaking" refers to the formation of a strongly bound and immobile layer of polymer that acts as a perfectly compatible interface to the film interior, effectively cloaking the film interior from the substrate. We emphasize that we do not mean to imply anything relating to the "screening" of van der Waals or any other type of potential interaction away from the substrate. The cloaking effect that we find in the film is akin to the cloaking phenomenon described in Ref. 35 for polymer-nanoparticle composites. Independence of T_g with nanoparticle volume fraction is commonly reported experimentally in composite systems when polymer-nanoparticle interactions are strong.[33] Thus, our findings reinforce the notion that the cloaking effect applies to both polymer composites and ultra-thin films.[7,51]

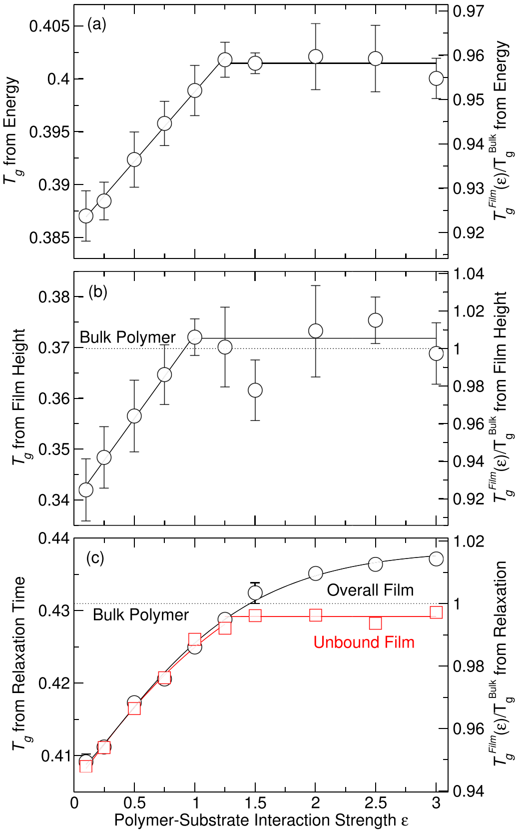

FIG. 8. (a) The glass transition temperature T_g defined from T dependence of energy (Fig. 1) as a function of the polymer-substrate interaction strength ε. T_g increases with ε up to $\varepsilon \approx 1.25$, a strength similar to the polymer-polymer interaction, and plateaus thereafter. (b) T_g defined from the polymer film height during heating as a function of ε. (c) T_g defined by a fixed relaxation time for both the overall and unbound films, as well as bulk polymer for comparison. For $\varepsilon > 1.0$, T_g of the unbound film is nearly an invariant of ε. This indicates the bound polymer "cloaks" the strongly interacting substrate. On the right side of all three panels, we normalize each definition of $T_g^{\mathrm{film}}(\varepsilon)$ by the corresponding glass transition temperature of the bulk polymer T_g^{bulk}. For panel (b), we use T_g^{bulk} defined by the T-dependence of density on heating.

In the limit large substrate interaction strength, the amount of bound polymer (characterized by A_b) should correspond to the amount of adsorbed polymer examined in recent experiments.[25,52] The experiments of Ref. 52 report that the amount of absorbed polymer saturates at large substrate interaction strengths, and we similarly find that the bound layer fraction A_b saturates at large ε. In addition, Ref. 25 finds a correlation between the amount of adsorbed polymer and the shift in T_g. Consistent with this finding, Fig. 9 shows that the our dynamically defined ΔT_g for the film as a whole has an approximately linear dependence on the amount of bound polymer A_b. In addition, we can test for a similar correlation between relaxation time and A_b, which has not been addressed thus far in the experimental literature. Thus, Fig. 9 also shows the relationship of

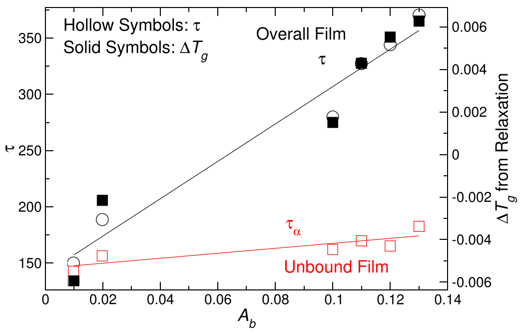

FIG. 9. The dependence of relaxation time at $T = 0.45$ (left vertical axis) and glass transition shift ΔT_g (right vertical axis) as a function of the fraction of bound polymer A_b. A correlation between ΔT_g or τ and A_b is apparent. The relaxation time τ_α of the unbound portion is essentially invariant with A_b, consistent with the cloaking of substrate interactions.

A_b to the relaxation time τ_α of the film interior or the overall film relaxation time τ. As anticipated from the data discussed above, the relaxation time τ_α of the unbound portion of the film is essentially invariant with A_b. In contrast, there is an approximately linear dependence on τ for the film as a whole with A_b, as we expect from the linear dependence of the dynamically defined T_g.

IV. CONCLUSION

We have studied supported coarse-grained polymer films with variable substrate interaction strength by molecular dynamics simulations. The thermodynamically defined glass transition temperature T_g is found to saturate to nearly a constant value for ε values greater than the polymer-polymer interaction strength, independent of the precise thermodynamic features that are used to extract T_g. However, the saturation value of T_g will generally be thickness dependent. In the case we study, the saturating value is close to the bulk, but this situation can differ for thinner films. We have also examined the change of dynamical behavior with substrate interaction strength and found a crossover interaction strength ε_c, above which the segmental relaxation near the substrate is significantly reduced. Unsurprisingly, ε_c is close to the polymer-polymer interaction strength. Above this threshold, we can separate the substrate bound polymer relaxation from the overall relaxation and show that T_g of the overall film (defined by a fixed relaxation time) increases with stronger substrate interaction strength, while the dynamically defined T_g of the unbound portion of the film saturates as substrate interaction strength exceeds the polymer-polymer interaction strength, similar to variations of T_g from the thermodynamic criteria. It is plausible that the slowing of the film dynamics induced by the substrate can exceed the enhancement of the dynamics at the free surface, leading to no change, or even an increase in T_g. Indeed, we do not see significant T_g reductions when the bound layer is present, consistent with Napolitano and co-workers.[53] This leads to the conclusion that a bound polymer layer may arise near the substrate of supported polymer films that "cloaks" the film interior from substrate interactions, resulting in small shifts in thermodynamic estimates of T_g from energy, film height, etc. In other words, since the relaxation time of this bound layer is so much larger than the film interior, it effectively acts as part of the solid substrate whose effective polymer-substrate interaction strength is similar to polymer-polymer interaction strength in the film interior. As a consequence, the changes in T_g no longer grow in proportion to the substrate interaction strength when such a bound layer forms. A similar result has been observed for polymer nanocomposites in Ref. 35. This "cloaking" effect near strongly attractive substrates and particles appears to be rather universal in systems having strong interfacial interactions.

SUPPLEMENTARY MATERIAL

See supplementary material for additional details on the thermodynamic definition of T_g, the influence of molecular mass on interfacial mobility gradient scale ξ, as well as the variation of relaxation time, non-ergodicity parameter, and stretching exponent.

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