Reconciling computational and experimental trends in the temperature dependence of the interfacial mobility of polymer films

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ABSTRACT

Many measurements have indicated that thin polymer films in their glass state exhibit a mobile interfacial layer that grows in thickness upon heating, while some measurements indicate the opposite trend. Moreover, simulations and limited measurements on glass-forming liquids at temperatures above the glass transition temperature T_g exhibit a growing interfacial mobility scale ξ upon cooling. To better understand these seemingly contradictory trends, we perform molecular dynamics simulations over a temperature regime for which our simulated polymer film enters a non-equilibrium glassy state and find that the relaxation time τ_{α} within the film interior, relative to the polymer–air interfacial layer, exhibits a *maximum* near the computational T_g . Correspondingly, we also observe that the interfacial mobility length scale exhibits a maximum near T_g , explaining the apparent reversal in the temperature dependence of this scale between the glass and liquid states. We show that the non-monotonic variation of ξ and the relative interfacial mobility to the film interior arise qualitatively from a non-monotonic variation of the gradient of the effective activation free energy of the film; we then obtain a quantitative description of this phenomenon by introducing a phenomenological model that describes the relaxation time layer-by-layer in the film for a temperature range both above and below T_g of the film as a whole. This analysis reveals that the non-monotonic trend in the relative interfacial mobility and ξ both arise primarily from the distinctive temperature dependence of relaxation in the interfacial layer, which apparently remains in local equilibrium over the whole temperature range investigated.

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I. INTRODUCTION

Numerous experimental and simulation studies have indicated that thin supported polymer films exhibit a mobile interfacial layer near their polymer–air interfaces.^{1–12} While most of these experimental studies characterize the mobile interfacial layer below the glass transition temperature T_g , ^{1–5,8} a study by Hesami *et al.*⁶ also shows the existence of the mobile interfacial layer well-above T_g . Some measurements show a mobile layer that grows upon heating in the glassy state^{3,4,8} with a length scale that is typically a few nanometers, while other measurements show a surface layer that is distinct from the bulk that grows on cooling in the glassy state^{1,2,13} with a length scale that is generally larger. These experimental

findings present a conundrum for explaining the behavior of the mobile layer near the free surface, both above and below T_g . Simulation studies of thin supported films indicate the existence of a mobile interfacial layer having a length scale of several nanometers, but the mobility scale in simulation studies of glass-forming liquids grows upon cooling toward T_g .^{9–12} The purpose of the present study is to help reconcile these contrary reported trends in the interfacial dynamics of cooled liquids and solid glass-forming materials through molecular dynamics simulations of a widely studied glass-forming polymer material over a wide temperature range. We note that the reversal of the temperature dependence of the interfacial mobility variation and interfacial layer thickness is also expected to occur in materials that crystallize. Specifically, the interfacial

mobility scale in crystalline materials, such as ice and nickel, grows beyond an onset temperature of about $(2/3)T_m$,^{14,15} where T_m is the melting temperature, and exhibits a scale that can be comparable to that of glass-forming liquids. In the liquid state, we expect these materials¹⁶ to exhibit a growing interfacial mobility and interfacial mobility scale upon cooling toward the melting temperature as in glass-forming liquids.^{14,15} The reversal of interfacial mobility relative to the interior of the solidifying material with free interfaces would appear to be a pervasive and practically important phenomenon.

To address this problem, we analyze the variations of the segmental relaxation time τ_{α} in the interfacial and film interior regions using the intermediate scattering function. Our analysis indicates that both the interfacial mobility relative to the interior and the interfacial mobility length scale ξ (defined by the thickness of the liquid-like mobile layer near the free surface) have maxima near the computational glass transition temperature T_g , at which our simulations go out of equilibrium. Our findings are consistent with experimental studies of the polymer films in their liquid and glass states.^{3,6,17} We gain insight into this phenomenon by using a simple mathematical model and show that this effect can be attributed to the different temperature dependence of relaxation time in the interior and free surface regions of the film. We also examine dynamic heterogeneity defined in relation to excessively mobile particles and find that the scale of the collective particle exchange motion,¹⁸ i.e., the string length L, does not exhibit a non-monotonic behavior entering the solid-like non-equilibrium "glass" state of the polymer film. This implies that the monotonic variation of the scale of the particle exchange motion that we observe is apparently not linked to the thickness of the mobile interfacial layer for polymer films in their glass state. This is in contrast to thin films above T_g , where evidence has been reported that ξ and the size of the exchange particle clusters ("cooperatively rearranging regions") are linked.¹

II. MODELING AND SIMULATIONS DETAILS

We use molecular dynamics simulations to study glass-forming thin polymer films. Polymers are modeled as chains of ten beads to model polymers free of the complication of chain entanglement.^{22,} Non-bonded monomers interact via a Lennard-Jones (LJ) potential, truncated and shifted at 2.5 σ (where σ is an LJ length parameter). All units are given in terms of strength ε and size σ of nonbonded polymer interactions. Therefore, T is given by $\varepsilon/k_{\rm B}$, where $k_{\rm B}$ is Boltzmann's constant, and time is given in units of $(m\sigma^2/\varepsilon)^{1/2}$, where m is the mass. We use these reduced LJ units throughout this work. Reduced units can be mapped to physical units with a size of chain segments $\sigma \approx 1$ nm-2 nm, time is in picoseconds, and $\varepsilon \approx 1$ kJ/mol. Neighboring monomers along a chain are connected by the finitely extensible non-linear elastic (FENE) potential^{22,23} with bond strength $k = 30\varepsilon/\sigma^2$ and range $R_0 = 1.5 \sigma$, values that are known to normally preclude crystallization of the polymer fluid.

We model the substrate as a collection of LJ particles. The LJ parameters for the possible combinations of interactions (e.g., *ss*, substrate-substrate; *ps*, polymer-substrate) are $\sigma_{ps} = 1.0$, $\varepsilon_{ps} = 1.0$, $\varepsilon_{ss} = 0.8$, and $\varepsilon_{ss} = 1.0$. 528 substrate particles are arranged in a triangular lattice [the (111) face of an FCC lattice]. The substrate particles

are tethered to these positions using harmonic springs of stiffness $k = 50\varepsilon/\sigma^2$. A purely repulsive wall defined by a "9–3" LJ potential to constrain the lower bound of the surface²⁴ is beneath the particle substrate. The size of the simulated film in the plane (*xy*-direction) is 20 × 20. We employ periodic boundary conditions parallel to the substrate and use 400, 480, and 600 polymer chains in the thin polymer film, resulting in a film that is ≈10, 12, and 15 monomers thick, where the thickness has a weak Arrhenius *T* dependence, as described in Ref. 10. Simulations are performed in an NVT ensemble (canonical ensemble) with a time step of 0.002. All simulations are performed using LAMMPS.²⁵

We determine the computational glass transition temperature T_g of the polymer film by heating at a fixed rate 10^{-5} deep in the glassy regime. At this heating rate, the glass transforms to an equilibrium fluid near T = 0.40 K, defined as T_g . To study the dynamics of the thin polymer film, we take configurations from the heating run and then extend the simulations at various fixed T. For $T \ge 0.40$ K, the polymer film is in equilibrium. Well below T = 0.40 K, the film is out of equilibrium, but the aging time scale is much larger than that accessible in our simulations so that potential energy remains nearly constant in the glass. At temperatures moderately below T = 0.40 K, the film thermodynamics exhibit aging on our simulation time scale. We characterize the film relaxation time τ_{α} using the self-part of the intermediate scattering function,

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

where q_0 corresponds to the first peak of the structure factor S(q) and $r_j(t)$ is the position of particle *j* at time *t*. We subsequently define the relaxation time τ_{α} by^{26,27} $F_s(q_0, t) = (1 - A)e^{-(t/\tau_s)^{3/2}} + Ae^{-(t/\tau_{\alpha})^{\beta}}$, where τ_s is the short vibrational time $\tau_s \approx 0.30$. We emphasize that τ_{α} at the computational glass transition T_g is much smaller, i.e., by about 8–10 orders of magnitude, than the α relaxation time at T_g defined by standard experimental methods. Below we designate the computational glass transition by T_g for economy of notation with an understanding that this temperature is distinct from the experimentally estimated glass transition temperature determined from the criterion that the structural relaxation time equals 100 s ("hundred second rule"). The difference in the T_g definition derives from the vastly different cooling rate in simulation and experimental studies of glass formation.

To characterize the relaxation time of different regions of the film, we follow a common description of the polymer film and a previous study.²⁰ We group the film into three regions: (i) a free surface layer, (ii) a middle layer, and (iii) a substrate layer. The free surface layer is defined by the top part of the film with a thickness of 3.5 σ ; the precise length we choose does not affect the qualitative trends we report. The substrate layer is defined by the layer near the substrate with a thickness of 4 σ . The middle layer is defined by the remaining part of the film (excluding the free surface layer and the substrate layer).

III. RESULTS

It is evident that the unusual behavior of the interfacial mobility scale ξ must be somehow determined from the gradient of the relaxation time within the film. Thus, we begin our analysis by

examining temperature variation of the relaxation time in the film interior and free surface to qualitatively characterize the mobility gradient near the free interface; this serves as a useful point of reference to understand the non-monotonic variation of ξ . We show the *T* dependence of the segmental relaxation time in the "free" (polymer–air) interface $\tau_{\alpha}^{\text{surface}}$ and the segmental relaxation time $\tau_{\alpha}^{\text{mid}}$ in the film interior region in Fig. 1(a). Relaxation in the interior of the film makes the largest contribution to the overall relaxation time of the film (at the film thickness we study), as inferred from the fact that the average relaxation time of the film as a whole is nearly indistinguishable from that of the film interior. The detailed definitions of middle and free interfacial layers, as well as their relaxation times (determined from a fit of our simulation data to the self-intermediate scattering function), are described in our previous work²⁰ and are briefly described in the section entitled Modeling and Simulations Details. We see that the *T* dependence of τ_{α} of the film closely tracks that of the film interior, and as in many computational and experimental studies, τ_{α} can be well-described by the Vogel-Fulcher-Tammann (VFT) expression, $\tau_{\alpha} \propto \exp[DT_0/(T-T_0)]$, under conditions where the film is in equilibrium. In the nonequilibrium glass state, the film exhibits an apparent Arrhenius T dependence with an activation energy less than that of the equilibrium system just before entering the glassy state, leading to a "kink" in τ_{α} at T_g . The relaxation time in the interfacial layer $\tau_{\alpha}^{\text{surface}}$ is



FIG. 1. (a) The relaxation time τ_{α} from $F_s(q_0, t)$ of thin polymer films as a function of inverse temperature 1/T for different regions and the film as a whole. The dotted vertical line indicates the crossover from equilibrium to glassy states and the computational glass transition temperature, T_g . The relaxation time of the free surface layer is fitted by the superposition of two Arrhenius relations in Eq. (4). Each Arrhenius regime is plotted as the dashed line. The relaxation time of the film interior clearly dominates the relaxation time for the film as a whole. (b) The ratio of the relaxation time (inverse mobility) in the interior and surface region, $\tau_{\alpha}^{\rm mid}/\tau_{\alpha}^{\rm surface}$. The solid orange line is the prediction from the mathematical model (detailed in the later part of this paper). The background color provides an indication of the crossover from equilibrium (red) to glassy (blue) states.

significantly smaller than that of the film interior, a phenomenon reported in many previous experimental and computational studies.^{6,28–32} In contrast to the film interior, the relaxation time near the free surface exhibits a nearly Arrhenius temperature at low T and shows no obvious "kink" symptomatic of the material going out of equilibrium. Previous experimental³¹ and computational²⁴ studies of the free surfaces of supported polymer films have reported that the interfacial relaxation can be described approximately by an Arrhenius function. Below we gain insight into the non-monotonic interfacial mobility relative to the film interior by assuming that the interior film dynamics can be described by a VFT expression at equilibrium, while the interfacial dynamics are well-described by a superposition of two Arrhenius relations, as evident in Fig. 1(a). We also fit the relaxation of the film interior to an Arrhenius relation under conditions where the film has gone out of equilibrium, following an experimental precedent^{3,17} and our own observations over an admittedly limited temperature range.

The relative mobility of the free surface to the film interior can be better understood by examining the ratio $\tau_{\alpha}^{\text{mid}}/\tau_{\alpha}^{\text{surface}}$. This quantity exhibits a maximum in Fig. 1(b) near the estimated computational glass transition temperature T_g , below which the film goes out of equilibrium for the cooling rate used here (10^{-5} , in reduced LJ units, LJ temperature/LJ time). Note that T_g is cooling rate dependent and differs significantly from T_g defined by experimental conventions, where the cooling rate is on the order of 1 K/min.

The consequence of the differing *T* dependence in the interior and free surface is that the ratio of the interfacial relaxation time increases with *T* below T_g and decreases with *T* above T_g . Both of these trends have been reported before experimentally,⁴ and the main purpose of the present paper is to understand this feature, along with the non-monotonic dependence of the interfacial mobility scale ξ .

We next describe how we extract the interfacial mobility scale ξ and the resulting *T* dependence as we pass through T_g . Following our previous work,^{10,12,19} we define the interfacial mobility scale ξ based on the relation,

$$\ln \tau_{\alpha}(z) = c \tanh\left[\frac{z-\xi_{\rho}}{\xi}\right] - \ln \tau_{0}, \qquad (2)$$

where ξ_{ρ} is the interfacial density scale, z is the distance to the substrate, and c and τ_0 are fitting parameters. This length scale ξ characterizes the thickness of the mobile layer near the free interface. Before we present ξ , we must also define an interfacial length scale governing the density variations (ξ_{ρ}) near a surface, which characterizes how "sharp" a polymer interface is and generally behaves quite differently from the interfacial mobility scale, ξ .^{12,19,27} We define the interfacial density scale ξ_{ρ} as the length at which the density in the interfacial layer reaches within 5% of the density of the film in the middle region.¹² The interfacial density scale ξ_{ρ} for various film thicknesses is illustrated in Fig. 2(a), where we observe that ξ_{ρ} varies linearly with T, similar to the density of the film as a whole,³³ and this quantity progressively increases with the film thickness. With our definition of ξ in hand, we proceed to examine the T dependence of the width of the mobile interfacial region ξ near the free boundary [Fig. 2(b)]. Since our units are defined in terms of a statistical segmental sizeon the order of 1 nm,³⁴ we see that the peak size of the



FIG. 2. (a) Interfacial density scale ξ_{ρ} of the polymer film as a function of temperature *T*. The interfacial density scale is monotonic: ξ_{ρ} grows upon heating. (b) Interfacial mobility scale ξ of the polymer film as a function of temperature *T*. The interfacial mobility scale is non-monotonic: ξ grows on cooling in the equilibrium regime, but in non-equilibrium states, ξ grows on heating, consistent with experiments by Ediger and coworkers (Ref. 4). The solid curve in the lower panel is a guide for the eye. The background color provides an indication of the crossover from equilibrium (red) to glassy (blue) states.

mobile interfacial region is also on the order of a few nanometers, where the peak in ξ occurs near T_g of the entire film. It is apparent that the thickness of the interfacial mobile layer also exhibits a non-monotonic variation with T and peaks near T_g . Our results for the temperature dependence of ξ in the glass state are qualitatively similar to the report of Ediger's group, although the criteria used in simulations to extract the interfacial scales are thought to be different than those in the fluorescence relaxation experiments.¹¹ Here, we show that despite the different definitions used in experiments and simulations, they qualitatively capture the same underlying behavior in the interfacial mobility scale. The growth of the thickness of the mobile interfacial layer below T_g upon heating is also notably similar to heated crystals.¹⁵ On the contrary, the thickness of the mobile interfacial layer grows upon cooling in the polymer film in its liquid state. Indeed, Hesami et al.⁶ observed a mobile interfacial layer in a polymer film at a temperature well-above T_g . The variation in the thickness of the mobile interfacial layer and the ratio of interfacial mobility relative to the film interior [Fig. 1(b)] then mirror each other.

We may obtain qualitative insight into the gradient of mobility by considering the dependence of the activation barrier for reorganization as a function of distance z to the supporting substrate. Based on a simple activation model, where $\tau_{\alpha} = \tau_0 \exp[\Delta G(T)/(k_{\rm B}T)]$, we can define the local activation free energy from the local relaxation as,

$$\Delta G(z,T) \equiv k_{\rm B} T \log \left(\frac{\tau_{\alpha}(z,T)}{\tau_0(z)} \right).$$
(3)

We see in Fig. 3 that $\Delta G(z, T)$ near the middle of the film increases on cooling, just as expected for the film as a whole. The gradient of the activation free energy near the free surface also increases upon cooling, but sharpens noticeably below T_g , in accord with the behavior found for ξ . We superimpose the *T* dependence of the interfacial mobility scale $\xi(T)$ on ΔG for each corresponding temperature; specifically, in Fig. 3, the red dots indicate the distance ξ to the free surface of the film at that temperature. Evidently, ξ tracks the position at which $\Delta G(z, T)$ tends to approach a plateau. The sharpening in the gradient in $\Delta G(z, T)$ near the free surface below T_g then follows the non-monotonic *T* dependence of ξ . Moreover, this representation clarifies that the gradient of mobility directly reflects the gradient in the activation free energy as a function of film depth.

To gain more quantitative insight into the non-monotonic behavior of the interfacial mobile length scale ξ , we construct a simple model describing the relaxation time gradient within the film both above and *below* T_g . The model is based on some reasonable premises from the observations of experiments and these simulations and rather standard phenomenological functional forms for the relaxation time as applied to relaxation layer-by-layer of the film: (1) Above T_g , the T dependence of the structural relaxation time of the film as a whole, τ_{α} , and of the film interior follows a VFT relation. (2) Below T_g (where the film is out of equilibrium), relax-ation exhibits a nearly Arrhenius T dependence [see Fig. 1(a)], a phenomenon observed in many materials upon entering the nonequilibrium glass state.^{17,35} (3) Relaxation in the polymer-air, or the "free" interfacial region, is inherently more rapid than that in the film interior so that the interfacial region can apparently equilibrate locally, even below the T_g of the film as a whole. Relaxation in this interfacial regime can be fit by a sum of two Arrhenius functions for high and low temperature regimes,

$$\tau_{\alpha}^{\text{surface}}(T) = \tau_0^{\text{H}} \exp(\Delta H^{\text{H}}/T) + \tau_0^{\text{L}} \exp(\Delta H^{\text{L}}/T), \quad (4)$$

where the superscripts H and L indicate the high temperature and low temperature regions, respectively, and ΔH represents the activation enthalpy. We also plot each Arrhenius relation as a dashed



FIG. 3. Local activation free energy ΔG as a function of distance to the substrate *z* for temperatures *T* ranging from 0.35 to 0.65 K. For each curve (temperature), we used red dots to indicate the length scale of the interfacial layer ξ . Specifically, red dots indicate the distance ξ to the free surface of the film at that temperature. The change in the behavior of ξ corresponds to the crossover to the glass state. The background color provides an indication of the crossover from equilibrium (red) to glassy (blue) states.

line to explicitly show their respective contributions in Fig. 1(a). Equation (4) appears to be valid over a T range where the film surface can equilibrate (which extends to a lower T than the range at which the interior can equilibrate). These qualitative observations are consistent with numerous previous experimental studies, indicating the existence of the mobile interfacial layer in thin polymer films.^{3–6,17,36} Notably, relaxation in this interfacial layer is fairly insensitive to film thickness, so this expression is expected to be quite useful in applications. Note that a single VFT relation could be used to describe the surface relaxation time, and such a model reproduces the qualitative features we report. However, the accuracy of a single VFT description is clearly inferior to the two exponential models we use.

In order to describe the relaxation time in the film interior as a function of temperature, we formalize the first two observations above and shed light on the origin of the non-monotonic variation of the ratio of the interfacial mobility to the film as a whole. We may express $\tau_{\alpha}(z, T)$ in the film interior as,

$$\tau_{\alpha}(z,T) = \begin{cases} \tau_0(z) \exp\left[\frac{D(z)T_0(z)}{T-T_0(z)}\right], & T > T_g(z) \\ \tau_0(z) \exp\left[\frac{\Delta H_g(z)}{T}\right], & T \le T_g(z), \end{cases}$$
(5)

where $T_g(z)$ is position dependent and again refers to the computational time scales we can access. We directly fit (5) layer-by-layer to our data for $\tau_{\alpha}(z)$ above T_g (see the definition in the text below), allowing us to determine the fragility parameter D(z), the VFT temperature $T_0(z)$, and the VFT prefactor $\tau_0(z)$ as a function of film depth z [see the supplementary material for the fit value of the VFT parameters D(z), $T_0(z)$, and $\tau_0(z)$]. As commonly observed for glassforming liquids, the VFT equation describes the relaxation time of the film as a whole and the film interior τ_{α} well. Below $T_g(z)$, the relaxation time in the film *interior* is described by the Arrhenius form¹⁷ of (5). The Arrhenius behavior of the film interior, with an apparent activation enthalpy $\Delta H_g(z)$, can be rationalized by recognizing that the activation barrier should not vary with temperature since the structure of the material is essentially fixed in the glass state. Importantly, this condition depends on the distance to the solid substrate. Requiring that Eq. (5) matches at $T_g(z)$ fixes the activation enthalpy in terms of VFT parameters,

$$\Delta H_g(z) = \frac{D(z)T_0(z)T_g(z)}{T_g(z) - T_0(z)},$$
(6)

so that ΔH_g is not a free parameter. Interestingly, this simple mathematical consistency argument predicts the activation enthalpy in its glass state based on observations on the fluid in its equilibrium state.

Figure 4(a) shows our results for the relaxation time $\tau_{\alpha}(z)$ (symbols) grouped into layers of thickness 0.875, as well as the fits to these data (lines) using Eq. (5). The relaxation time of the entire film and in the middle of the film changes rather abruptly as a function of T when the film goes out of equilibrium near T_g (i.e., an approximate "kink" in the relaxation time). This depth dependent T_g for each layer demarks the switch from VFT to Arrhenius behavior, and we illustrate the variation of $T_g(z)$ in Fig. 4(b).

As expected, $T_g(z)$ decreases approaching the free interface of the film since it is more mobile, and we cannot define a value for $T_g(z)$ for the three layers nearest to the free surface. Figure 4(b) also

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FIG. 4. (a) The relaxation time τ_{α} of a thin monolayer of the polymer parallel to the substrate as a function of inverse temperature 1/T. The solid line is from the model, and solid dots represent the relaxation time from simulation for the layer that is at *z* distance to the substrate. For the free surface layer (z = 12.7, 13.6, and 14.4), the relaxation time is described by Eq. (4). The free surface region exhibits a different temperature dependence because this part of the film apparently remains in equilibrium over the *T* range we simulate, and this part of the film must accordingly be modeled separately. The background color provides an indication of the crossover from equilibrium (red) to glassy (blue) states. (b) T_g (black) and ΔH_g (red) as a function of distance to the substrate *z*.

shows the $\Delta H_g(z)$, which similarly decreases near the free interface. Evidently, the length scale of the variation of $\Delta H_g(z)$ near the free interface is smaller than that of the local $T_g(z)$. Near the film's free surface [see curves labeled z = 12.7 or greater in Fig. 4(a)], we show that the *T* dependence of the relaxation time $\tau_{\alpha}^{\text{surface}}$ is described by the superposition of two Arrhenius functions [Eq. (4)]. We interpret these phenomena as arising from a relief of the packing frustration in the interfacial region, an interpretation discussed before by Riggleman *et al.*³⁷ in connection with a discussion for glass formation to become more Arrhenius in thin films with free interfaces. We note that the Arrhenius behavior should not be confused with the socalled "strong" glass-formation behavior—as the latter requires both Arrhenius *T* dependence as well as an activation energy $\approx 14RT_g$, where *R* is the molar gas constant.

Overall, our simple model captures the variation of the mobility gradient as a function of *T*. Accordingly, we are now in a position to use this model to better understand the non-monotonic *T* dependence of the interfacial mobility ratio, $\tau_{\alpha}^{\text{mid}}/\tau_{\alpha}^{\text{surface}}$, reported in Fig. 1(b). The solid orange line in Fig. 1(b) is obtained from our model and accords with the simulation data. Specifically, we evaluate $\tau_{\alpha}^{\text{mid}}$ and $\tau_{\alpha}^{\text{surface}}$ by integrating Eq. (5) over their respective film regions. Generally speaking, aging will increase τ_{α} of the interior, but will not affect the quasi-equilibrium mobile surface layer; this should lead to an increase in the magnitude of the relaxation time ratio in Fig. 1(b). Additionally, aging should push T_g to lower temperature. We can capture such a behavior simply by an *ad hoc* reduction in T_g in our model, which we find that it results in an increase in the peak in the mobility ratio (see the supplementary material). We expect this model to be useful for applications in 3D printing and other systems, where the existence of the mobility gradient in thin films as a function of temperature has technological importance.

Finally, we consider how the interfacial mobility scale ξ might relate the scale of collective motion within the glass-forming film. Computational studies of the thickness of the mobile interfacial layer in supported films suggest that ξ varies linearly with the extent of the polymer segment exchange motion, ¹⁹ i.e., string length L at temperatures above T_{g} . We provide a detailed description of the determination of the string length in the supplementary material. In many cases, the string length L can be identified with the scale of hypothetical cooperative rearranging regions (CRR) of Adam-Gibbs (AG).^{33,38,39} Although the role of collective motion is not the emphasis of the present paper, we examine the T dependence of the extent of cooperative motion L in Fig. 5 to determine if it tracks the nonmonotonic T dependence of the interfacial mobility scale ξ as the system enters the non-equilibrium glassy state, given that previous simulations have suggested that these scales are directly linked phenomenologically.^{11,19,20} Evidently, the correlation between L and ξ does not extend into the glass regime, given that L does not decrease below T_g . Our results for the temperature dependence of L below T_g are qualitatively consistent with the findings by Forrest and Mattsson,¹ in the sense that both works indicate that the scale of cooperative motion (distinct from the interfacial layer scale) continues to grow on cooling in the glassy state. Although the change in τ_{α} of the film as a whole (and the film interior) can be quantitatively understood from the variation of the activation barrier for relaxation,²⁰ this expression evidently does not apply to materials out of equilibrium. We may use this finding to gain insight into the observed relaxation in the interfacial layer, which we argued above remains in local equilibrium. If this hypothesis is true, then the string length in Fig. 5 should continue to describe relaxation in the interfacial layer. In the supplementary material, we show that this is the case to a good approximation. This situation calls into question whether the relation between relaxation and thermodynamic properties (such as the configurational entropy and the corresponding string length³⁹) can be relied upon in materials far out of equilibrium.



FIG. 5. The string length L as a function of temperature T for polymer films. The background colors provide an indication of the crossover from equilibrium (red) to glassy (blue) states.

IV. CONCLUSIONS

We used molecular dynamics simulations to help understand the apparent differences in the temperature variations of the thickness of the mobile interfacial layer in supported thin polymer films. Our findings indicate that the interfacial mobility near the polymerair interface grows upon cooling for fluids under equilibrium conditions. Consistent with many experiments,^{3,4,8} this trend reverses in the non-equilibrium glass state so that ξ grows upon heating. Indeed, our approach to quantify the mobile surface layer effectively defines this layer as a liquid-like layer, similar to the experimental reports of Paeng et al.^{3,4} The physical trends we observe imply that the thickness of the interfacial mobile layer ξ peaks at temperature near the glass transition T_g , where the film goes out of equilibrium. We also show that the non-monotonic variation of the interfacial mobility length scale is closely related to the gradient in the activation free energy near the free surface. Building on the observations of experiments and simulations, we construct a simple model using standard functional forms for fitting relaxation time data (i.e., VFT and Arrhenius functions) to gain insight into the non-monotonic variation of the interfacial mobility length scale ξ . This layer-bylayer model of the relaxation time within the film quantitatively captures the mobility gradient evolution with the film as a function of temperature T and distance to the substrate z, and we are able to reproduce the peak in the mobility gradient and interfacial mobility scale upon passing through the glass transition temperature T_g of the film.

The consistency of the behavior of ξ below T_g from our simulations and many experiments does not account for other experimental observations that suggest a growing scale for the interfacial region on cooling in the glass state,^{1,2,13} which bears further consideration. Forrest *et al.*¹ inferred a growing interfacial scale on cooling in freestanding polymer films based on an assumption that the interfacial scale is directly related to the scale of collective motion in the film in the glass state. While there is a support for a relation between the interfacial mobility scale and the scale of cooperative motion from simulations above T_g ,^{11,19} our present work indicates that this correlation does not hold in the glass state [see Figs. 2(b) and 5]; thus, it is not clear what the results of Ref. 1 imply about the interfacial scale. On the other hand, Pye et al.² also found a growing interfacial mobility scale upon cooling through physical aging experiments and did not rely on an assumed relation between interfacial and cooperativity scales. Their findings present an interesting conundrum when compared to our findings and those from Ediger's group.³ Fortunately, Roth¹³ has already considered this puzzle and suggested that the interfacial mobility scale from aging experiments measures the fraction of the film exhibiting a non-bulk-like aging dynamics, which is distinct from a mobile interfacial layer. Since the measurements by Paeng et al.³ probe the scale of the most mobile liquid-like portion of the film, this will reflect the portion of the film with little or no aging.8 Indeed, the scales of the aging experiments are about two times larger than those of the mobile surface layer. Generally speaking, it is natural to expect that such different measurement methods have different sensitivities to the often large relaxation gradients in the thin polymer films.

The interfacial dynamics of the supported polymer film in the non-equilibrium glass state have some distinctive properties from the film in its equilibrium viscous liquid state above T_g . In the glass

state, we observe a thin mobile interfacial layer similar in thickness and temperature variations to crystalline materials approaching their melting temperature. ^{14,15,40} The thickness of this layer (≈ 3 nm) in this region is largely insensitive to film thicknesses over the range of film thickness and temperatures investigated. The temperature dependence of the structural relaxation time $\tau_{\alpha}^{\text{surface}}$ of this interfacial layer can be described by a superposition of two Arrhenius functions. These observations of the free interfacial layer of supported polymer films are consistent with the experimental observations of Yang *et al.*³¹ on thin unentangled polystyrene films, both above and below the glass transition temperature. However, the behavior of the film relaxation in the interior differs when crossing over from VFT behavior in the equilibrium region to an Arrhenius behavior below T_g . Interestingly, our simple model for the T dependence of the relaxation time provides an estimate of the activation enthalpy ΔH_g in the glassy film interior based on equilibrium VFT parameters. We also find that our previous treatment of relaxation in thin polymer films in terms of collective motion only applies to the film under equilibrium conditions, which means that only the film interfacial layer can be described by this model at temperatures below T_g of the film as a whole. Accordingly, we model the temperature dependence of the film interfacial layer differently from the film interior.

SUPPLEMENTARY MATERIAL

See the supplementary material for VFT fitting parameters and description for the string-like cooperative motion and its relation with the interfacial relaxation time.

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