Dynamic phase transitions in freestanding polymer thin films

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Edited by Pablo G. Debenedetti, Princeton University, Princeton, NJ, and approved August 31, 2020 (received for review April 10, 2020)

After more than two decades of study, many fundamental questions remain unanswered about the dynamics of glass-forming materials confined to thin films. Experiments and simulations indicate that free interfaces enhance dynamics over length scales larger than molecular sizes, and this effect strengthens at lower temperatures. The nature of the influence of interfaces, however, remains a point of significant debate. In this work, we explore the properties of the nonequilibrium phase transition in dynamics that occurs in trajectory space between high- and low-mobility basins in a set of model polymer freestanding films. In thick films, the film-averaged mobility transition is broader than the bulk mobility transition, while in thin films it is a variant of the bulk result shifted toward a higher bias. Plotting this transition's local coexistence points against the distance from the films' surface shows thick films have surface and film-center transitions, while thin films practically have a single transition throughout the film. These observations are reminiscent of thermodynamic capillary condensation of a vapor–liquid phase between parallel plates, suggesting they constitute a demonstration of such an effect in a trajectory phase transition in the dynamics of a structural glass former. Moreover, this transition bears similarities to several experiments exhibiting anomalous behavior in the glass transition upon reducing film thickness below a material-dependent onset, including the broadening of the glass transition and the homogenization of surface and bulk glass transition temperatures.

T
here are numerous applications of ultrathin amorphous films, including flexible integrated circuits (1), tissue engineering (2), and semiconductor manufacturing (3). However, after more than 25 years of study, the dynamics of amorphous ultrathin film materials are still not well understood. As film thickness (h) decreases in systems with weak substrate interactions, the glass transition temperature (Tg) in both polymeric and small-molecule glass films drops by 15 K to 30 K (4–10). This effect is more substantial in freestanding polystyrene films where decreases of up to 70 K are reported independent of molecular weight (11–13). In the thick film limit (h > h0, ≈ 30 nm) or when one probes time scales shorter than ~1 s where the confinement effects are relatively modest, the changes in Tg can be understood as a consequence of a mobile layer propagating from the free surface into the film (14).

However, reducing film thickness below h0 and probing longer time scales causes several new features to emerge. Measurements of the gradient of Tg (∇Tg) in supported polystyrene films indicate that the changes in Tg cannot be explained as a film with a bulk-like Tg being supplanted by a surface layer with a lower glass transition temperature (Tg,s = Tg − ΔT) as h decreases (15). While Tg,s ≪ Tg in thick films, Tg,s anomalously increases dramatically upon reduction of h until it joins the film-averaged Tg for h < h0. At this point, the Tg measured at the surface can no longer be distinguished from that of the entire film. In the case of freestanding polystyrene films, the suppression of ∇Tg occurs through the film-averaged Tg decreasing with h (16). In contrast, Tg,s, remains constant. For h < 2h0, Tg,s and Tg join and continue to decrease with h. These significant results suggest that the film dynamics as a function of the distance from the interface homogenize for thin films.

While it is conceivable that having a distinct surface and bulk Tg that converge to a single value upon reduction of h would lead to a narrowing of the glass transition, this view does not agree with results in supported thin films with weak substrate interactions. In these cases, the reduction of ∇Tg is accompanied by a broadening of Tg for both polymeric and molecular glass films, suggesting the material still samples a broad distribution of dynamics in ultrathin films (9, 10). This transition occurs in two stages. As h decreases in thick films, the lower Tg onset decreases independent of the constant bulk-like upper Tg onset, suggesting an increasing amount of fast modes are becoming available due to the effect of the free surfaces. For h < h0, these lower and upper onsets decrease sharply and in parallel, implying that bulk-like dynamics begin to disappear at this length scale. The dynamics of freestanding and supported polymer films have been studied directly using the dynamics of fluorescent dye molecules and demonstrate the emergence of a fast decay process independent of the single, slow decay process available for thick films (17, 18). This population of fast decaying processes may account for the increased dynamic heterogeneity in thin films.

These corresponding transitions indicate a qualitative difference in the dynamics of glassy films below h0, but an explanation for these transitions remains elusive. Molecular dynamics simulations have studied the mobility of ultrathin films extensively in

Significance

As a bulk supercooled liquid approaches the glass transition temperature, spatiotemporal fluctuations in dynamics increase by orders of magnitude. While this effect is fundamental to the glass transition, few have studied how confinement affects this dynamic heterogeneity. Here, we examine this effect in thin films through the lens of the dynamic phase transition from high- to low-mobility dynamic states in a set of model freestanding thin films. We find that changes in this dynamic transition are similar to deviations in thermodynamic transitions under confinement due to capillary condensation. Furthermore, these changes are reminiscent of several atypical features of the glass transition observed in ultrathin film experiments, suggesting a possible link between our simulations and experiments.

R.J.S.I. and R.A.R. designed research; R.J.S.I. performed research; R.J.S.I. contributed new reagents/analytic tools; R.J.S.I. analyzed data; and R.J.S.I. and R.A.R. wrote the paper. The authors declare no competing interest.

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This article contains supporting information online at https://www.pnas.org/lookup/suppl/doi:10.1073/pnas.2006703117/-/DCSupplemental.

First published October 2, 2020.

www.pnas.org/cgi/doi/10.1073/pnas.2006703117

PNAS | October 13, 2020 | vol. 117 | no. 41 | 25407–25413
The fastest rate typically used in experimental cooling rate-dependent \( T_0 \) measurements is \( \sim 1 \) K s\(^{-1}\). At this cooling rate, \( T_0 \) only weakly depends on \( h \) (9), while the longest timescale reached in direct simulations of glassy solids is \( \sim 1 \) \( \mu \)s (24, 25). Moreover, while many of these molecular dynamics studies focus on the average local relaxation time on the approach to a film’s interface, we have not found a study that looks at the spatiotemporal fluctuations of the dynamics in ultrathin films. This oversight seems conspicuous considering that this is a fundamental feature of bulk supercooled liquids on approach to the glass transition (26) and given the widening distribution of relaxation rates seen in thin-film experiments.

One approach to studying dynamic heterogeneity in bulk glasses is the use of space- and time-integrated dynamic order parameters defined over entire trajectories. This approach contrasts with equilibrium thermodynamics that uses configurational order parameters. A typical dynamic order parameter may count trajectories using periodic boundary conditions in all directions and mod- ify Anderson’s algorithm so that it is run in the NPT ensemble at a pressure of \( P = 0 \). We generate trajectories by harvesting configurations every \( \Delta t \) at \( T = 0.5\) e/k\(_B\), we also simulate bulk trajectories using periodic boundary conditions in all directions and modify Andersen’s algorithm so that it is run in the NPT ensemble at a pressure of \( P = 0 \). We generate trajectories by harvesting configurations every \( \Delta t \).

**Methods**

In this work, we model oligomeric bead-spring polymers each with 10 beads of diameter \( r \) and mass \( m \). The nonbonded interactions are taken via a Lennard-Jones potential with a well depth of \( \epsilon \) that is truncated at 2.5\( r \), and the bonded interactions are taken via a finite extensible nonlinear elastic potential (41). We study systems of \( N = 1,250 \) monomers at two temperatures: \( T = 0.5\) e/k\(_B\) and 0.48\( e/k_B\). At each temperature, we simulate two ensembles of freestanding films, thick films with \( h = 20\)\( \mu \)m and thin films with \( h = 12.5\)\( \mu \)m, in the NVT ensemble with a timestep of \( \delta t = 0.002\)\( \tau_0 \) where \( \tau_0 = \sqrt{m\pi^2/\epsilon} \) is the unit Lennard-Jones time scale. The temperature is maintained through an Andersen thermostat (42) using a massive stochastic collision every \( \Delta t = 656\)\( t_0 \). At \( T = 0.5\) e/k\(_B\), we also simulate bulk trajectories using periodic boundary conditions in all directions and modify Andersen’s algorithm so that it is run in the NPT ensemble at a pressure of \( P = 0 \). We generate trajectories by harvesting configurations every \( \Delta t \).

**Global Dynamic Transition**

We begin our analysis by considering the average value of our mobility order parameter \( K [x] \) at a given field strength \( K = \langle K [x] \rangle \). To better visualize this order parameter’s behavior, we plot the difference between the mean mobility at \( s \) and its equilibrium value \( \Delta K = K - K_0 \) for \( T = 0.5\) e/k\(_B\) and 0.48\( e/k_B\) in Fig. 1 A and B. We include plots of \( K_0 \) in SI Appendix, Fig. S1. The \( \Delta K \) plots show sigmoidal behavior in all cases. We include plots that demonstrate this behavior sharpen with increased observation time, consistent with previous investigations in the bulk in SI Appendix, Fig. S2 (29). This result indicates that the sigmoid behavior will sharpen into a discontinuous transition with, coexisting points, \( s = s^* \), in the large system limit \( (N, t_{obs} \rightarrow \infty) \). Thus, we are observing a first-order trajectory phase transition in \( K [x] \). This transition is equivalent to a fat tail in the \( \Delta K [x] \) probability distribution in equilibrium \( (P_0 (\Delta K [x])) \) at low \( \Delta K [x] \) compared to the expected Gaussian, as shown in Fig. 1 A and B, Insets. Larger versions of these insets are in SI Appendix, Fig. S3. These insets reveal that low-mobility trajectories become less probable under confinement, and the low-mobility tails of the distribution become more Gaussian in ultrathin films.

Next, we analyze the susceptibility of our \( K [x] \) order parameter

\[ \chi_s = -\frac{\partial K_s}{\partial s} = (K [x] - K_0)^2, \]

where \( K_s \) is defined as

\[ K_s = \frac{1}{N_{obs}} \sum_{j=1}^{N_{obs}} \Delta t_j (\tau_j - \tau_j'), \]

\[ \text{with } \tau_j = \{ r(t) \}_{1 \leq s \leq N \leq s + \tau_0}, \]

is a trajectory, \( t = \Delta t \) is a time within \( x \), and \( \Delta t_j (\tau_j - \tau_j') = ||r(t') - r(t)|| \) is the distance a monomer \( j \) travels between times \( t \) and \( t' \) within \( x \). Here, \( r(t) \) is the position of particle \( j \) at time \( t \) within \( x \), and we take \( N_{obs} = t_{obs}/\Delta t \) to be the number of observed frames within \( x \).

This order parameter has been shown to exhibit a dynamic phase transition in the bulk (29) and has been linked to a dynamic transition from a state with a large number of particle hops (large \( K [x] \)) to a state with a small number of particle hops (small \( K [x] \)) (31). Following refs. 29 and 44, we may now consider the probability distribution of trajectories at a fictitious field \( s \) that is linearly coupled to this order parameter

\[ P_s [x] = P_0 [x] e^{-K_s [x]} \]

in which \( P_0 [x] \) is the equilibrium probability distribution of trajectories and \( P_s [x] \) is the probability distribution of trajectories at a given field strength \( s \). We could obtain this distribution at all \( s \) by generating a sufficient number of trajectories in the equilibrium distribution \( (s = 0) \), this is not computationally efficient because of the rarity of the low-mobility (small \( K [x] \)) trajectories at the temperatures at which we perform our experiments. Instead, we perform Monte Carlo in trajectory space, transition path sampling (TPS) (45), at multiple values of \( s \). All averages are calculated using the multistate Bennett acceptance ratio (46). We implement replica-exchange Monte Carlo across windows in \( s \) (47) and use waste recycling (48, 49) to enhance our sampling. Obtaining converged statistics requires more than \( 10^8 \) trajectories across all windows in \( s \) for a given \( (h, T) \) combination. Complete simulation and TPS details can be found in SI Appendix.
Fig. 1. Evidence of changing dynamics in amorphous thin films. In all plots, the gray, blue, and red curves correspond to the bulk, thick film, and thin film results. Error bars show bootstrap error across our two configurations and are indicated by the shaded regions. (A and B) Average space–time mobility order parameter minus the equilibrium mobility \( \Delta K_s = K_s - K_0 \) as a function of field strength at two temperatures, \( T = 0.50 e/k_B \) and \( 0.48e/k_B \). The sigmoidal behavior in these plots demonstrates a first-order dynamic phase transition. This transition indicates fat tails in the equilibrium probability distribution of the our dynamic order parameter \( \Delta K_s = K_s - K_0 \) compared to the expected Gaussian distribution (black dashed lines), as shown in the insets. Increased confinement reduces this deviation from Gaussian behavior, suggesting decreased spatiotemporal dynamic heterogeneity in thin films. (C and D) Susceptibility, \( \chi_s \), at all confinements. These plots demonstrate that confinement shifts the peak in \( \chi_s \), a finite-sized estimate coexistence point of the dynamic transition \( s^\ast \), to higher field strengths. They also demonstrate a rounding of the thick film transition, which becomes sharper with increased confinement. (E and F) Alpha-relaxation times \( \tau_s \), measured as the time at which the self-intermediate scattering function averaged at a field strength of \( s \) intersects \( 1/e \). We plot local relaxation times \( \tau_s \) for \( z = 6\sigma \) away from the interface as dashed lines for both film thicknesses. The thick and thin film lines track each other until \( \tau_s \) of each film sharply increases near its respective coexistence point. If the changes in \( \tau_s \) were described by overlapping dynamic gradients, we would expect that a sharper increase in \( \tau_s \) occurs in thick films as the thin film begins to transition to compensate for the homogenization of the thin film. Instead, \( \tau_s \) in the thick film increases less sharply. We do not include error bars in the inset or local relaxation rate plots for clarity.

which we plot in Fig. 1 C and D. Considering the peak of this function to be the finite system estimate of the coexistence point \( s^\ast \) between high- and low-mobility phases, we find that low temperatures have decreased \( s^\ast \) and sharper peaks compared to high temperatures, as seen in ref. 29. These changes in \( s^\ast \) indicate changes in equilibrium dynamic behavior, with lower values of \( s^\ast \) indicating more significant deviation from Gaussian, consistent with the behavior in Fig. 1 A and B. Insets. We also find \( s^\ast \) increases with increasing confinement at both temperatures. Again, this effect is related to the more Gaussian distribution of thin films’ dynamics demonstrating decreased low mobility fluctuations. We also observe that the thick film has a broader transition than the bulk or thin film. This broadness is consistent with thick films falling out of dynamic equilibrium in stages rather than all together.

This dynamic transition corresponds to a dramatic increase in the alpha-relaxation time \( \tau_{\alpha} \) defined as the time at which the self part of the intermediate scattering function evaluated at a field strength \( s \),

\[
F_s(t) = \left\langle \sum_j \frac{\sin(q\Delta r_j(t', t + t'))}{Nq\Delta r_j(t', t + t')} \right\rangle_{t', s},
\]

intersects \( 1/e \), as shown in Fig. 1 E and F. Here we take \( q = 6.96\sigma^{-1} \). While this increase is evident in all instances, the growth in the films’ relaxation rates is significantly less than the apparent relaxation rate of the bulk in the low-mobility, inactive phase. Thus, although the films can reach a low mobility dynamic phase, the effect of this phase on the relaxation rates appears to be significantly lessened.

We also plot the local alpha-relaxation time \( \tau_{\alpha}(z) \) a distance of \( z = 6\sigma \) from the free surface for the thick and thin films in Fig. 1E. While these curves track each other for small fields
A close-up of the same profiles. When both films reach the inactive state \((s = 0.013\sigma^{-2}\Delta t^{-1})\), mobility profiles again overlap.

To further investigate this effect, we show the local mean mobility as a function of field strength minus the equilibrium local mean mobility for a selection of distances from the interface \(z (\Delta K_r(z) = K_r(z) - K_0(z))\) in Fig. 3 A and B for thick and thin films, respectively. At each \(z\), our local order parameter \(\Delta K_r(z)\) exhibits a clear sigmoidal transition associated with a local dynamic phase transition. These plots illuminate two trends with \(z\). First, the decrease in dynamics at the local coexistence points \((s^*(z))\) decays on approach to the surface, indicating the active and inactive basins are moving closer together. Second, these local transitions’ coexistence points shift smoothly as a function of \(z\) in the thick film. In the thin film, these transitions occur at a similar high \(s^*\) throughout the entire film except for the plane closest to the free surface.

We can see the homogeneity in the thin film transition more clearly by plotting \(s^*(z)\) in both the \(h = 20\sigma\) and 12.5\(\sigma\) films in Fig. 4 A and B for \(T = 0.5\epsilon/k_B\) and 0.48\(\epsilon/k_B\), respectively. We extract this value by fitting the profiles in Fig. 3 to the sum of a linear function and a hyperbolic tangent at each \(z\). In each case, it appears that the thick films have two distinct transitions: one on the interior of the film and one at the interface with a

\[
K_r(z) = \frac{\Delta t}{\sqrt{2\pi\delta^2}} \sum_{i=1}^{N} \sum_{j=1}^{N} \Delta r_j (t_{i-1}, t_i)^2 e^{-z_j^2 (t_{i-1}, t_i)^2 / 2},
\]

where \(z_j(t)\) is the shortest distance of monomer \(j\) to the interface at time \(t\). We find that our results are qualitatively insensitive to the choice of \(\delta\) so long as \(\delta \leq 0.05\sigma\). For each trajectory, we treat the interface as the slab that the local film density reaches \(1/2\) its average interior value. We start by examining the average value of the local dynamics at a given field strength \((K_r(z) = \langle K_r(z) \rangle_z)\) for thick and thin films at \(T = 0.5\epsilon/k_B\) in Fig. 2. As is typical in simulations of freestanding films, we find an increase in mobility as measured by \(K_r(z)\) near the free surface. Similar to other simulation results, we find the dynamics of the equilibrium systems \((s = 0)\) are nearly identical in the thick and thin film cases. As \(s\) increases, however, the profiles of our local mobility order parameters in thick and thin films differ. At \(s = 0.008\sigma^{-2}\Delta t^{-1}\), the \(h = 20\sigma\) films experience a substantial decrease in the mobility in the films’ center while a smaller change occurs in the dynamics of the \(h = 12.5\sigma\) films. As we increase field strength to \(s = 0.011\sigma^{-2}\Delta t^{-1}\), we find thick films’ mobility profile from 2\(\sigma < z < 4\sigma\) joins the thin films’ mobility profile while separation still occurs in the centers of the films.
smooth transition between the two, and this is consistent with the broadening of the susceptibility peak for the thick films shown above in Fig. 1. For thin films, this splitting of the surface and interior transitions dramatically decreases ($T = 0.5k_B$ or $0.48k_B$), indicating that sufficiently thin films only have a single transition that has a coexistence point near that of the surface transition in the thick films. This observation demonstrates that, while the equilibrium distribution of local dynamics in thick films transitions from being very non-Gaussian at the film’s center to slightly non-Gaussian at the film’s surface, the equilibrium distribution of local dynamics in thin films is homogeneously slightly non-Gaussian throughout the film.

We now investigate whether we can describe the merging of the surface and bulk transitions with a simple model in which we assume the dynamics in a thin film as simple linear combinations of the enhanced mobility at each interface. To do this, we assume that we can write the local mobility in the $h = 12.5\sigma$ films as a linear combination of the local mobility in the $h = 20\sigma$ films from both interfaces, which are distances $z$ and $12.5\sigma - z$ away from the $h = 12.5\sigma$ films. Here, we suppose that interfaces in $h = 20\sigma$ films are separated enough to leave local mobil-
fluorescence dye rotation measurements of ref. 17 that show the persistence of a bulk relaxation mode coexisting with a fast mode in freestanding films as thin as 14 nm remains an outstanding question. This bulk process is particularly unexpected because coarse-grained simulations of thin freestanding films, including ref. 22 and our thin films in Fig. 1E, show deviations from bulk behavior in relaxation times in the films' centers at this level of confinement. Given that the mobile free surface layer is expected to grow upon cooling, this would suggest even more significant deviations from bulk behavior in experiments that regularly reach significantly larger timescales and higher mobility gradients. Our biased film-averaged intermediate scattering functions logarithmically decay in the caged region rather than exhibiting a two-step decay (SI Appendix, Fig. S5). Noting that the dynamic phase transition leaves the film’s surface relaxation rates nearly unaffected (SI Appendix, Fig. S6), we speculate that using a longer observation time may lead to such a separation of timescales and that the fast mode may be interpreted as a layer near the free surface, while the rest of the film exhibits bulk-like fluctuations into the low-mobility phase.

The homogenization of the transition point in thin films also provides further evidence of interfacial tension between the active and inactive phases studied herein. However, we emphasize that these results do not require a view of the glass transition through the lens of dynamic facilitation (34). Given that it is known that the inactive phase preferentially samples low-energy states (53) with locally preferred packing motifs (32), we cannot rule out the possibility that our results are a manifestation of the predicted interfacial tension between amorphous states predicted from the RFT model (54). Some attempts at describing the dynamics near free surfaces have relied on accounting for simple changes in the number of particles forming a cage near the free surface (55) and propagating this effect into the film (56). Our results suggest that it may be important to take into account the spatial variation in the materials’ ability to sample low-energy amorphous states and the interfacial energy between them. This accounting would manifest as a term that penalizes the formation of large gradients in mobility and not a simple additive effect of the two interfaces involved, as shown in Fig. 4A and SI Appendix, Fig. S6. As emphasized above, it will be of interest to observe how this manifests in films with asymmetric and competing boundary conditions.

Data Availability. Code to run transition path sampling simulations and analysis of trajectories have been deposited in Open Science Framework at http://doi.org/10.17605/OSF.IO/TG7V3. Some study data are available.

ACKNOWLEDGMENTS. We thank Zahrak Fahkraai and Sanat K. Kumar for helpful discussions regarding experimental work and wetting transitions in thin-film materials, and Connie B. Roth for helpful discussions. This work was supported through the University of Pennsylvania Materials Research Science and Engineering Center (DMR-1720530), including its shared computational equipment facility. This work also benefited from computational resources provided through Extreme Science and Engineering Discovery Environment allocation DMR-150034.