



Disconnecting structure and dynamics in glassy thin films

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Nanometrically thin glassy films depart strikingly from the behavior of their bulk counterparts. We investigate whether the dynamical differences between a bulk and thin film polymeric glass former can be understood by differences in local microscopic structure. Machine learning methods have shown that local structure can serve as the foundation for successful, predictive models of particle rearrangement dynamics in bulk systems. By contrast, in thin glassy films, we find that particles at the center of the film and those near the surface are structurally indistinguishable despite exhibiting very different dynamics. Next, we show that structure-independent processes, already present in bulk systems and demonstrably different from simple facilitated dynamics, are crucial for understanding glassy dynamics in thin films. Our analysis suggests a picture of glassy dynamics in which two dynamical processes coexist, with relative strengths that depend on the distance from an interface. One of these processes depends on local structure and is unchanged throughout most of the film, while the other is purely Arrhenius, does not depend on local structure, and is strongly enhanced near the free surface of a film.

machine learning | glass | thin film

Confinement of glassy materials to nanometric length scales leads to striking changes to their microscopic dynamics and consequently to their material properties (1). Direct observations in both experiments and simulations find exponentially more particle rearrangements near the free surface of a film (2–5), as well as position-dependent aging rates within the film (6, 7). A key question is whether enhanced dynamics near a free surface (or suppressed dynamics near a substrate) are connected with changes in the local structural environment of the rearranging particles.

A direct connection between a particle's local structural environment and its propensity to rearrange has been established in bulk glasses in the last several years (8–12). In these systems, machine learning methods have proven remarkably successful in identifying optimal linear combinations of local structural features—termed “softness” and denoted S_i for particle i —to predict particle rearrangements (13). For Lennard-Jones (LJ) mixtures, softness can be represented as a weighted integral over the local radial distribution function $g_i(r)$ (14). This measure has been shown to be over an order of magnitude more predictive of rearrangements than measures such as the local potential energy or coordination number (*Supporting Information* and ref. 14) and has yielded new insight into the physics of glassy systems (15, 16). In particular, it was shown that, for a system at temperature T , the probability that a particle of softness S at time t will rearrange at time t has the form

$$P_R(S) = \exp(\Sigma_0 - e_0/T) \times \exp[(\Sigma_1 S - e_1 S)/T] \equiv P_I(T)P_D(S, T), \quad [1]$$

where $P_I(T) = \exp(\Sigma_0 - e_0/T)$ and $P_D(S, T) = \exp[(\Sigma_1 S - e_1 S)/T]$. The constants Σ_0 , e_0 , Σ_1 , and e_1 are independent of S and T ; it follows that $P_I(T)$ is purely Arrhenius and is independent of softness (15). $P_D(S, T)$ depends on softness but is purely Arrhenius at each value of S . As a result, the average soft-

ness, $\langle S \rangle$, is directly predictive of the relaxation time of supercooled liquids (15) and aging bulk glasses (16). Non-Arrhenius relaxation arises from changes in $\langle S \rangle$ with temperature. We take this decomposition of the non-Arrhenius behavior of the supercooled system into a collection of locally Arrhenius processes to be a strong indication not only that S_i is a strong predictive quantity but that it is capturing important features of glassy physics. In bulk systems, it is therefore now clear that dynamical slowing down near the glass transition is intimately associated with structural changes.

Here we show that softness provides a useful, quantitative framework to analyze glassy thin films. As for the binary LJ mixture, we show that the probability of rearrangement has the form of Eq. 1 in every layer of the film. However, the enhancement of dynamics near the surface stems solely from $P_I(T)$; $P_D(S, T)$ does not depend on position in the film. We confirm that our results are robust to the specifics of the softness calculation. Indeed, we find that, for a very general set of quantities that characterize the local structural environment surrounding a particle, there is no combination of these quantities that can distinguish between parts of the film with very different dynamics. The enhanced dynamics near a free glassy surface are therefore fundamentally different from the dynamics in the rest of the film: Near free surfaces, relaxation is dominated by mechanisms that are independent of local structure.

Methods

Our model systems are composed of short-chain polymers, specifically Kremer–Grest chains, each with $N = 20$ beads of diameter σ . The nonbonded interaction is an attractive, truncated LJ potential, and the intrachain bonds are stiff harmonic springs. This model has a bulk glass (dynamic cross-over) transition temperature of $T_g = 0.44 \pm 0.01$ as determined by constant cooling rate experiments (7); defining the transition as the temperature at which the bulk relaxation time reaches $\tau_\alpha = 10^4$ leads to $T_g \approx 0.423$ (17). Following

Significance

Do glassy dynamics depend strongly on local structure? In bulk systems, a quantitative answer to this question exists and is affirmative. The dynamical behavior of nanometrically thin glassy films is strikingly different from bulk systems, and it is natural to ask whether this difference stems from local structural differences. Using machine learning techniques, we show that altered dynamics near an interface do not stem from changes of local structure near the interface. Rather, the dynamics depend on the simultaneous occurrence of two independent processes, one that depends on structure but not position within the film, and an Arrhenius process that does not depend on structure but depends sensitively on position.

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the protocols in refs. 7, 17, and 18, which characterized many structural and dynamical properties of thin glassy films as a function of thickness, temperature, and age for this model, we prepared both freestanding films and films on frozen amorphous substrates with thickness of order 30σ in a box of fixed volume, V . For the supported films, the substrate was taken to be a slice of an independently equilibrated sample of the same polymer model at $T = 0.425$; these chains were frozen in place, and the polymer–substrate interactions were taken to be identical to the polymer–polymer interactions. Here, \hat{z} is normal to the film surface. The systems were simulated using the HOOMD-blue package (19, 20) in the NVT ensemble with a time step of $\delta t = 0.001\tau$, where τ is the LJ unit of time. All configurations were prepared at an initial reduced temperature of $T = 0.8$ and cooled at a constant rate of $\Gamma = 1 \times 10^{-3}$ to the desired temperature; the aging time t_{age} refers to simulation time subsequent to the end of this cooling procedure. While this cooling rate is very fast relative to experimental quenches, and the time scales accessible in simulations are short when expressed in physical units, we are nevertheless able to observe key features such as glassy dynamics and altered interfacial mobility in our thin film simulations. Additional details can be found in [Supporting Information](#).

Although we have chosen a particular polymer model for this study, we expect that our findings generically apply to fragile glass formers. At the time scales of segmental relaxation that govern glassy dynamics, polymeric and small-molecule glasses are fundamentally similar (1). The softness results we obtain in the center of the film are qualitatively in excellent accord with earlier results for bulk Kob–Andersen (KA) systems (14–16), so chain connectivity is not responsible for differences in the behavior of thin films and bulk systems that we observe [although important polymeric effects are known to exist in glassy films, particularly for high-molecular-weight samples (21)]. We find that, in thin-film KA systems, the two sphere sizes tend to segregate near the interface, and it is difficult to determine whether the changing dynamics near the interface is a direct result of these structural changes or not. By studying a model system where this is not an issue, we are able to determine that altered microscopic structure is not necessary for altered interfacial dynamics.

The machine learning approach we use, support vector machine (SVM) with a linear kernel, is physically transparent, corresponding to a straightforward classification problem. We begin by following the methodology of ref. 15, and first study S_j . The goal is to find a combination of local structural features that distinguishes particles that are likely to rearrange in the future from those that are unlikely to rearrange. We begin by recording many particle trajectories, either from within 5σ of the center of mass of an aged thin freestanding film at $T = 0.425$ or from a bulk system at the same temperature. We identify particle rearrangements using a “hop” indicator function, $p_h(i; t)$ (22). To define $p_h(i; t)$ for a particle i at time t , we first specify two time intervals $A = [t - 5\tau, t]$ and $B = [t, t + 5\tau]$; the hop indicator function can then be expressed as

$$p_h(i; t) = \sqrt{\langle (r_i - \langle r_i \rangle_B)^2 \rangle_A \langle (r_i - \langle r_i \rangle_A)^2 \rangle_B} \quad [2]$$

where $\langle \rangle_A$ and $\langle \rangle_B$ denote averages over A and B intervals. From the p_h trajectories of the particles, we identify a “training set” of 2,000 particles that are about to rearrange, such that $p_h > p_c = 0.2$ in the subsequent frame, and 2,000 particles that have not rearranged for a long time, where $p_h < p_{c,l} = 0.007$ for many hundred τ . We have verified that selecting the training set particles either from bulk simulations of the model or from the center of simulated films does not influence the results that follow. We note, however, that the definition of p_h could obscure the contribution of smoother particle motions to structural relaxation.

Given this training set, we then measure many different quantifications of the local structure for each of the particles in our training set, and embed each particle in a high-dimensional space (where each dimension corresponds to one of the measures of local structure). We characterize the local environment of each particle in the training set using a number, M , of “structure functions,” G_α , where α indexes the structure function type. In ref. 15, we showed that we could limit our structure functions to local, coarse-grained versions of the pair correlation function,

$$G_r(i; r, \sigma) = \frac{1}{\sqrt{2\pi}} \sum_{j \in \mathcal{X}} e^{-R_{ij} - r^2 / 2\sigma^2}, \quad [3]$$

where R_{ij} is the distance between particles i and j , \mathcal{X} is the set of particles near particle i with $R_{ij} < 2.5\sigma$, and $r \in [0.9, 1, 1.1, \dots, 2.5]$. The machine learning algorithm then simply tries to classify the “soft” (likely to rearrange) and “hard” (unlikely to rearrange) particles in the training set by finding the linear combination of structure functions that best separates the two populations of particles.

To find the optimal linear combination of structure functions, we embed the particles in our training set in the space of structure functions, \mathbf{G}_i , and find the hyperplane in \mathbb{R}^M that best separates the two classes (a nonlinear kernel would find the best hypersurface). Softness is the signed distance to the plane: $S_j = \mathbf{w} \cdot \mathbf{G}_j + b$, where \mathbf{w} is the hyperplane normal and b is the bias; the physical meaning is captured in \mathbf{w} , and we use b to simply set the average value of softness $\langle S \rangle = 0$ at some reference temperature. We have shown that, in the supercooled regime, 90% of the rearranging particles in bulk LJ mixtures have $S_j > 0$ (15).

One difference in protocol compared with ref. 15 is that here we use snapshots of thermalized configurations of the particles, rather than looking at energy-minimized “inherent structures.” We thus avoid spurious rearrangements due to thermal contraction from the finite temperature glass to the zero-temperature state of the film, at the cost of some loss of predictive accuracy due to fluctuations of particles within their cages, which contribute to fluctuations in S_j . Nevertheless, we find that our predictive accuracy remains high, with more than 80% of rearranging particles identified as soft (i.e., with $S_j > 0$) (14, 15) for bulk systems as well as for particles in the center of the film. We have verified that our qualitative conclusions are insensitive to choices made, such as using the choice of additional structure functions (bond-angle-dependent functions (13) or spherical harmonics coarse-grained in the radial direction).

We previously found that, in bulk systems, increasing the range over which these structure functions extend does not significantly increase the correlations that we find between structure and dynamics, suggesting that, at least in the bulk, the nonlocal contributions to particle relaxation are small (or that these structure functions are poor at distinguishing interesting structural features at farther distances). We note that it is straightforward to apply our approach directly to, e.g., granular and colloidal experimental systems (13), and it is, in fact, more straightforward to compute the G_r than to calculate, e.g., the local free volume of a particle.

Results

We compare the dynamical properties of thin films with spatially resolved values of particle softness. Fig. 1 shows several quantities as a function of position in the film, where $z = 0$ at the center of the film. We plot the density $\rho(z)$ relative to its value at the center of the film, $\rho(0) - \rho(z)$ (black dotted line); the upturn at $|z| \approx 16$ corresponds to the downturn in the density at the edge of the film. The softness, defined so that the average softness vanishes at the center of the film (blue solid line), remains flat until it comes within 2.5σ of the edge of the film. Recall that the cutoff distance for structure functions that enter into softness is 2.5σ ; the upturn in softness therefore reflects the drop-off in density at the edge of the film.

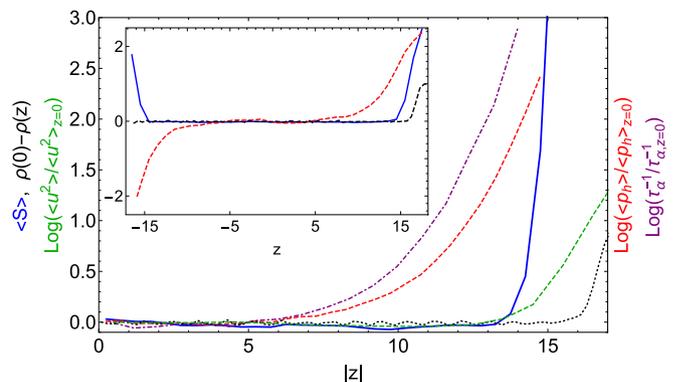


Fig. 1. From left to right, the curves show $\log(\tau_\alpha^{-1}(z)/\tau_\alpha^{-1}(0))$ (purple dot-dashed curve), $\log(p_h(z)/p_h(0))$ (red dashed curve), $\langle S(z) - S(0) \rangle$ (solid blue curve), $\log(DW(z)/DW(0))$ where DW is the local Debye–Waller (DW) factor (green dashed curve), and density profile $\rho(0) - \rho(z)$ (black dotted curve). All data are for a freestanding thin film at $T = 0.425$ and $t_{age} \approx 5 \times 10^5$ ($\tau_\alpha, z=0 \approx 2.2 \times 10^4$). (Inset) Spatial profile of mean softness (blue solid curve), \log of normalized $\langle p_h \rangle$ (red dashed curve), and density profile $\rho(0) - \rho(z)$ (black dashed curve) for a supported film at $T = 0.45$ and $t_{age} \approx 6 \times 10^5$ ($\langle p_h \rangle_{z=0} \approx 0.27$).

We have also plotted two measures of the long-time dynamics in the film, the logarithms of the averaged hop indicator $\langle p_h(z) \rangle$ (red dashed line in Fig. 1) and the α relaxation time $\tau_\alpha(z)$ (purple dot-dashed line). We extract $\tau_\alpha(z)$ from the decay of the overlap function (23) within each layer. These show a notable enhancement even quite far from the edge of the film, down to about $|z| \approx 7$.

We call particular attention to the regime between $|z| = 7$ and $|z| = 13$ in Fig. 1. In this regime, we find that the mean softness is flat even while the dynamics speed up by an order of magnitude; in a bulk system, these large differences in dynamics would correspond to a shift in average softness to $\langle S \rangle \approx 0.4$, well outside any noise in our measurement of the mean softness. These results show clearly that the enhanced surface dynamics are not associated with a change of softness.

Some studies have found that the local DW factor—the mean-squared displacement of particles at a time comparable to τ —provides a good correlator of longer-time mobility in both bulk samples and thin films (24, 25). We find that this does not hold in our model; consistent with the finding of ref. 3, the length scale associated with an average enhancement of the local DW factor (green short-dashed line in Fig. 1) remains short (of order 2σ to 3σ) even as the enhanced mobility (red short-dashed and purple dot-dashed lines) extends deep into the film. Additionally, we have directly quantified the accuracy of using the local DW factor to predict rearrangements according to the p_h measure described in *Methods*; using an optimal cutoff on the value of the DW factor, we find that only $\sim 75\%$ of rearranging particles are correctly identified in the bulk system. This is less than the predictive accuracy of softness of 80% , which is particularly surprising in light of the fact that the DW factor is computed using a subset of the dynamical information used to define rearrangements via p_h . We take this as strong evidence of the robustness of our measurements of local structure and their connection to glassy rearrangement dynamics.

Fig. 1, *Inset*, reports results for a film at $T = 0.45$ that is supported by an amorphous substrate. Here the dynamics are exponentially suppressed near the solid interface and enhanced at the free surface. However, the value of $\langle S \rangle$ shows no indication of a difference in the local structural environment of the particles; again it remains flat, except within 2.5σ of the surfaces. To treat both sides symmetrically, we do not include substrate particles in calculating the structure functions; the upturn in softness is therefore associated with the loss of particle density on both sides. We note that amorphous walls have been used to detect point-to-set-like length scales (5, 26), but these structural length scales are short enough ($\sim \sigma/2$ in KA mixtures) to fall inside the 2.5σ range of the structure functions, and are buried in our analysis by the effects of density loss for particles near the substrate.

Fig. 1 thus tells us that the enhanced/suppressed dynamics near a free/solid surface decay from the surface with a length scale that is not reflected in the softness: The softness is flat throughout the film except very close to the edge, where it rises due to the decrease in the density of the film there.

One possible explanation for this discrepancy between dynamics and structure in the film is facilitation. Enhanced dynamics at the very edge of the film could lead to enhanced dynamics deeper into the film as rearrangements facilitate other rearrangements. To test this idea, we turn to the “softness propagator” introduced in our earlier study of bulk binary LJ systems (15). Consider a set of particles that all have softness S_0 at $t = 0$ and calculate $G(S, S_0, t)$, the distribution of S of these particles at a time t . This propagator describes the process by which the softness of a particle i evolves due to rearrangements of nearby particles; for example, particles with softness less than zero evolve toward higher softness with time as nearby rearrangements alter local structure. Eventually, the distribution $G(S, S_0, t)$ must approach the equilibrium distribution of S at sufficiently long times t . The

propagator therefore captures the physics of facilitation. Here we compute averages over this propagator,

$$\langle S(t) \rangle_{S_0} = \int SG(S, S_0, t) dS. \quad [4]$$

In bulk KA systems, the average softness of particles with initial softness S_0 evolves toward the mean of the softness distribution on approximately the scale of the α -relaxation time (16) for all S_0 . Here we compute this quantity in a layer-resolved way, with the results shown in Fig. 2. To collect sufficient statistics, we average over particles, and we define “center” and “edge” by taking slices of the film of width 4σ . While there are modest systematic differences in how quickly softness relaxes toward the mean of the distribution, these are very small compared with the almost order of magnitude difference in the mean relaxation time of particles in these two slices of the film. From the facilitation picture, one would expect $\langle S(t) \rangle_{S_0}$ in a given layer to decay on the time scale of the relaxation time in that layer. Fig. 2 shows that this is not the case: $\langle S(t) \rangle_{S_0}$ decays on the scale of the relaxation time of the bulk system for particles anywhere in the film, even those near the surface. We therefore see no evidence of facilitation: Although particles near the surface are rearranging at a considerably higher rate than in the bulk, particularly for soft particles, those rearrangements are not facilitating changes of softness nearby at an enhanced rate. The enhanced rearrangements near the surface are apparently ineffective in changing softness (or, equivalently, the structure).

Facilitation might alternately arise if there were stronger spatial correlations in softness near the surface, so that soft particles were more likely to lie near other soft particles. As a first effort to detect these subtler effects, we introduce a different class of structure functions. Since, in the bulk, softness itself is a good predictor of mobility, we first compute the softness of every particle as described above. We then compute the local softness densities at different distances from each particle,

$$G_S(i; r, \sigma) = \frac{1}{\sqrt{2\pi}} \sum_{j \in \mathcal{X}} S_j e^{-(R_{ij}-r)^2/2\sigma^2}. \quad [5]$$

These structure functions capture radial features of the softness field itself. Inclusion of these structure functions slightly increases our predictive accuracy (Fig. S3), but nevertheless fails to distinguish positions within the film. Again, this result suggests that a straightforward facilitation picture does not explain enhanced dynamics near a free surface. While we have shown

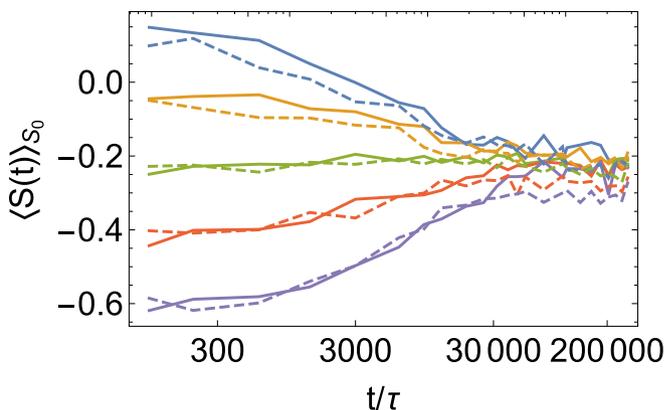


Fig. 2. Time evolution of softness for particles, in bins of softness, for different layers of a $T = 0.425$, $t_{\text{age}} \approx 5 \times 10^5$ film. Solid lines correspond to averages over particles with $|z| < 4\sigma$, and dashed lines correspond to particles in the range $8\sigma < |z| < 12\sigma$. At $t = 0$, all particles whose softness values are ± 0.2 of S_0 are included in the average.

that the above structure functions are not useful for understanding thin film dynamics, we speculate that adding these functions to the usual set in the bulk might allow generalized versions of softness to predict the intermediate time and length scale phenomena associated with dynamical heterogeneities, which appear to be well described by simple facilitated models (22, 27).

Taken together, our results imply that the rapidly changing dynamics near interfaces cannot be attributed to local structural changes. We therefore ask the simpler question of whether the local structural environment of a particle depends in any way on the particle's position in the film. To answer this, we directly perform supervised learning on the position of a particle using SVM with linear and Gaussian kernels as well as feed-forward neural networks with up to six fully connected layers (see *Supporting Information* for details), focusing on the freestanding films described above ($T = 0.425$ and $t_{age} \approx 5 \times 10^5 \tau$). Instead of training on whether particles are rearranging or not, we construct a training set consisting of “central” particles (with $|z| < 1.25$) and edge particles (with $11.0 < |z| < 12.25$, i.e., close to the edge but still more than 2.5σ from the density fluctuations near the film boundary). The relaxation time in the central layer is $\tau_\alpha \approx 2.2 \times 10^4$, while that in the edge layer is $\tau_\alpha \approx 6.5 \times 10^3$. Can we distinguish between these two sets of particles using local structure alone?

To capture many different aspects of the local structural environment, we expand our set of structure functions beyond the purely radial ones used above. We include isotropic spherical harmonic bond orientational order functions, G_{Q_l} (15, 28). We also use a collection of spherical harmonics, $G_{Y_{lm}}$, using z as the axis of symmetry. This is potentially quite important, as the structure functions should reflect the symmetry of the underlying system itself. We compute the G_{Q_l} and $G_{Y_{lm}}$ for even l (up to $l_{max} = 12$) in shells of thickness $\sigma/2$; explicit definitions are given in *Supporting Information*. Training on 2,500 particles from each class, we find cross-validation accuracies of 50%; that is, we are completely unable to distinguish particles in different layers of the film using this very general set of radial and angular structure functions. Thus, not only softness but any measure of local structure is independent of position everywhere in the film except within the cutoff distance of its edge.

We now show that, although softness itself does not explain enhanced dynamics near a free surface, formulating the problem in terms of softness yields valuable insight. We have first verified that Eq. 1 holds for thermalized particle configurations in our polymer system in the bulk, suggesting that the physics is quite general. This is shown in Fig. 3, *Inset*, where there is a clear exponential dependence of relaxation time on inverse temperature for different values of S .

As shown in *Supporting Information*, we find that the probability of rearrangement for different softness also displays an Arrhenius temperature dependence in every layer of the film. Fig. 3 uses a layer-by-layer analysis to plot the softness-dependent $\ln P_D$ and softness-independent $\ln P_I$ contributions to the rearrangement probability as a function of position within the film. We find that P_D is completely insensitive to film position (consistent with the inability of softness to distinguish position within the film), whereas P_I is strongly affected by the interfaces. As shown in Fig. S7, the increase in P_I near the free surface can be attributed to both a decreasing energy barrier e_0 , and a decreasing multiplicity Σ_0 as defined in Eq. 1 (*Supporting Information*); that P_I increases despite the competing effects of e_0 and Σ_0 indicates the importance of the drastically reduced energy barriers near the free surface. Importantly, the length over which this change occurs is not generic—it depends on both film temperature and aging—and therefore does not correspond to a simple multiplicative reduction in the barrier height as a function of distance from the interface. This clearly demonstrates the crossover from one relaxation mechanism to the other. That energy

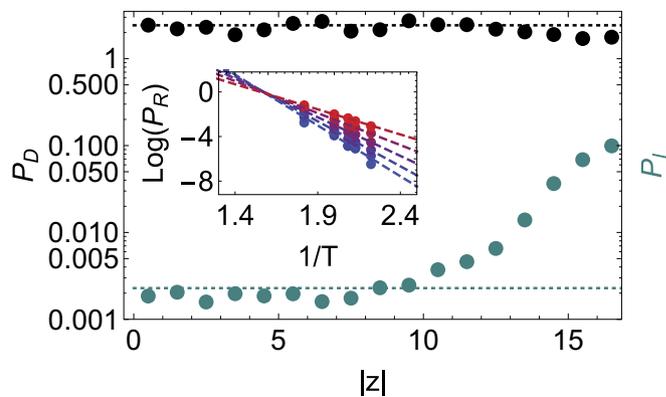


Fig. 3. Values of P_D (upper, black points) and P_I (lower, teal points) as a function of position within a freestanding thin film at $T = 0.425$ and $t_{age} \approx 5 \times 10^5$, derived from the $P_R(S)$ curves in *Supporting Information*. Dashed lines correspond to the bulk values of these quantities obtained by fitting $P_R(S)$ vs $1/T$ for $S = -2, -1, \dots, 1, 2$ for bulk samples prepared at different T and zero pressure (shown in *Inset*, with the blue-to-red (bottom-to-top) scale going from $S = -2$ to $S = 2$). Although there are small deviations of the softness-dependent terms very close to the edge of the film, these are small compared with the large enhancement of the softness-independent terms. This enhancement persists on a length scale matching the enhancement of dynamics seen in Fig. 1.

barriers can be strongly affected by interfaces and result in a “fluid” phase even well below T_g is consistent with recent experimental work on glassy film dewetting (29).

We note that P_I and P_D depend on the cutoff length characterizing the structure functions chosen, since we know that structure functions with a range somewhat larger than our maximum cutoff here do add slightly to the predictive value of softness in the bulk (15). However, the extremely modest dependencies we expect are not enough to account for the dramatic changes observed in, e.g., Fig. 3.

Discussion

In conclusion, we have applied machine learning methods to show that the relaxation dynamics in glassy thin films are characterized by two independent processes, one that depends on local structure but not position in the film and one that is purely Arrhenius and depends on position in the film but not softness. Moreover, there is no detectable correlation between structure and enhanced or suppressed dynamics near the surfaces of thin glassy films. This is true even after radically enlarging the space of local structure quantities we consider to very general classes of two-point and multipoint quantities. Although we cannot consider all possible structural quantities, our results strongly suggest that the local structure is the same everywhere except very close to the edge of the film.

Note that, in other simulation models of glass formers, it is well known that some structural features can persist farther away from the surface into the film (e.g., density oscillations or species segregation in multicomponent LJ fluids). Our results show that long-ranged dynamic mobility gradients can exist even in the absence of any such structural features, suggesting that the altered dynamics near interfaces are likely not primarily structural in nature.

We note that we are limited to using structure functions with a truncated spatial range $L = 2.5\sigma$. One might ask whether our conclusion that local structure is uniform throughout the film is an artifact of having chosen a value of L that is too small to characterize the structure of a cooperatively rearranging region. If that were the case, our results would imply that the core of the cooperatively rearranging region, of size L , would have to be independent of position in the film. Thus, any dependence on

position would have to come from the structure (but not the density) of the outer corona of the cooperatively rearranging region. This seems highly unlikely.

Existing theoretical models of the behavior of thin glassy films start from a diverse set of assumptions, considering configurational entropy, facilitated dynamics, and the effect of changing elastic moduli on the barriers to local rearrangements (24, 30–35). Our results strongly favor theoretical descriptions that do not rely on structural differences to propagate the effect of the interface into the film. Moreover, the results in Figs. 1 and 2 show that one cannot simply conclude that enhanced dynamics are a consequence of facilitation: Even in thin films, there is a strong connection between local structure and dynamics, but interfaces provide an additional source or sink of mobility that somehow does not affect the rate at which local structure (softness) relaxes.

The behavior of thin glassy films has often been interpreted in terms of a two-population model, in which there is a glassy, immobile layer near the center of the film and a liquid-like mobile layer near the free surfaces (1, 36–38). This interpretation is supported by observations of probe molecules embedded in films (39, 40). Our results show that the two populations are indistinguishable, from a structural point of view. We note that previous studies have observed a decoupling between some measures of local structure, for instance the local free volume (25), and thin film dynamics. Our approach does not just add an additional data point in this direction; it rules out whole

classes of potential local structural descriptors: Any local feature that could be written as a linear, or even nonlinear, combination of the structure functions used in this work is invalidated by this study.

Instead, our results show that the two populations are distinguished by two different and uncorrelated mechanisms of relaxation, which must coincide in order for rearrangements to occur. One of these processes, P_D , depends on structure, and the other process, P_I , does not. If these processes could independently cause rearrangements, then we would expect $P_R(S, T) = P_I(T) + P_D(S, T) - P_I(T)P_D(S, T)$ instead of $P_R(S, T) = P_I(T)P_D(S, T)$; our observations are consistent with the latter form, not the former. This surprising finding is buttressed by the decoupling between the physical relaxation time scale and the softness relaxation time scale observed in Fig. 2. Interfaces primarily affect dynamics through P_I . It is tempting to speculate that P_I is related to recent observations of a decoupling between surface diffusion and activated relaxation events in glass thin films (41, 42).

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