nature portfolio

Peer Review File

Linking Long-range Surface-Induced Mobility Enhancement and Intrinsic Fragility of Polymer Glasses

Corresponding Author: Professor Ophelia Tsui

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
This manuscript by Nie et al investigates the connection between surface-induced mobility enhancement and intrinsic fragility in polymer glasses. Using stress relaxation experiments on a series of polymers spanning a broad range of fragilities, the authors show that both the nanoscale mobile layer thickness (h_t^{nano}) and the microscale propagation length (h_t) increase monotonically with bulk fragility. Complementary coarse-grained molecular dynamics simulations qualitatively reproduce the experimental trends and suggest that enhanced surface mobility propagates into the bulk via shear-like excitation modes whose penetration depth depends on fragility.
The combination of macroscopic mechanical measurements and simulations is a strong aspect of the study, and the correlation between fragility and propagation length is intriguing and potentially impactful. Overall, the manuscript is of high interest for the glass and polymer physics community, so I strongly recommend considering for publication, after revision. The following comments are intended to further clarify and strengthen the presentation and interpretation.

1) The analysis of thin film data relies on a simplified Heaviside-step model for the depth-dependent relaxation time $\tau(z)$. While this provides a convenient parametrization and yields good fits, the physical meaning of a sharp discontinuity in $\tau(z)$ deserves further discussion.
First, the extracted values of h_t^{nano} and h_t depend directly on this assumption. It would be useful to comment on the robustness of the conclusions with respect to smoother profiles (e.g., tanh). A brief discussion clarifying that the monotonic correlation with fragility does not depend critically on the sharp step assumption would significantly strengthen the manuscript.
Second, the use of single relaxation times and linear (arithmetic) averaging of $\tau(z)$ may be nontrivial in systems with broad distributions of relaxation times. Since fragility is intrinsically related to the breadth and temperature sensitivity of relaxation spectra, it is reasonable to ask whether a Heaviside profile could partly reflect representing a smoother $\log \tau(z)$ gradient on a linear τ scale. In other words, is the apparent bilayer a physical discontinuity, or could it arise from viewing a continuous distribution in linear τ? In the latter case, what would be the upper bound on the intrinsic width of the transition region consistent with the data?

2) The identification of the fast mode ($\tau 1$) with the mobile surface region is well motivated and supported by the agreement between $\tau 1$ and $\tau 0$, as well as comparison with literature α-relaxation times . While their interpreation is physically-sound, the authors should avoid overinterpreting and consider that other relaxation modes (e.g., interfacial mechanical effects, heterogeneous stress distributions, beta or gamma relaxations, slow Arrhenius process) could also be involved.

3) A central finding of this manuscript is the correlation between the nanoscale mobile layer thickness and (reduced) fragility. While normalization of fragility values facilitates comparison between experiments and simulations, the physical meaning of a ratio of fragilities is not entirely straightforward. Since fragility is defined as the slope of $\log \tau$ (and not linear τ, to reiterate on the previous comments) versus T_g/T at T_g, it is already a dimensionless measure of kinetic sensitivity. The authors should clarifying what additional physical insight is gained by plotting m normalized by that of PVC, and how the reader should interpret m/mPVC beyond simple rescaling.

In addition, the fragility values obtained in the coarse-grained simulations differ substantially in absolute magnitude from experimental values (in the SI, I read values around 20, which in real conditions are basically Arrhenius dependendes). Given this discrepancy, it may be too strong to imply that the simulated PVC quantitatively represents real PVC. It may be

more precise to state that the simulations are performed on model polymer systems with systematically varied fragility, which reproduce the qualitative experimental trends. I think this change would actually add more "universality" to the claims (see limitations of this statement in the last comment).

4) The discussion interprets the propagation length ht primarily in terms of bulk fragility. However, previous work by the main author and by other groups (e.g., Polymer 51, 5309 (2010)) has shown that the fragility of surface layers can decrease relative to the bulk. This raises an interesting conceptual question: if the surface region is less fragile than the bulk, yet the present mechanism relies on bulk fragility to control long-range propagation, how are these observations reconciled? Is the shear-mediated propagation discussed here fundamentally governed by bulk dynamical properties, even if the local surface fragility differs? Or does the mechanism implicitly assume that the relevant “driver” is the surface-bulk dynamic contrast rather than absolute fragility values? A brief discussion clarifying whether in the view of the authors the process is mediated primarily by bulk dynamics, surface dynamics, or their contrast is needed.

5) The manuscript presents fragility as a unifying parameter governing both nanoscale mobility enhancement and long-range propagation. Within the investigated systems, the monotonic correlation between h_t, h_t^nano and fragility is clearly demonstrated, and this is a strong point. However, the studied polymers are all linear systems with relatively narrow dispersity (at least for PS, upper limit of 2 for PVC) and without strong specific interactions.
It would therefore be advisable to moderate the universality claims. Fragility often correlates with other material parameters that may also influence surface mobility propagation, such as chain stiffness, chemical architecture, cohesive energy density, Poisson’s ratio, shear modulus, entanglement density, molecular weight, dispersity, ... Since these variables are not independently varied in the present dataset, fragility may partly act as a proxy for a broader set of structural and mechanical properties. Explicitly acknowledging that the framework has been validated for a specific class of linear polymer glasses, and that extension to branched, crosslinked, strongly associating, or network systems remains to be explored, would frame the conclusions more precisely without diminishing their impact.

Reviewer #2

(Remarks to the Author)
In this work, the authors report a correlation between polymer glass-former fragility and the thickness of a near-surface layer with dynamics that differ from bulk behavior. The manuscript proposes a mechanistic picture in which increasing fragility leads to increased dynamic heterogeneity, which in turn sets the thickness of the anomalous surface layer. I have several comment I would encourage the authors to address before I can recommend this article for publication:

Comments:

1. The model used to fit the data in Fig. 1C already assumes a bilayer profile, so the bilayer structure is imposed by the fitting rather than emerging as a prediction from the data. In particular, the Heaviside-type transition seems to be part of the model rather than something uniquely supported by the measurements. Visualizing the data in Fig. 1C with a log-scale y-axis and providing a quantitative assessment of fit quality, especially for thinner films would be helpful.

2. Fig. 3A appears to suggest that the thickness of the layer with enhanced-dynamics for PVC is approximately 724/2 nm (half of the film thickness at which bulk-like relaxation mode disappears). This seems inconsistent with the values reported in Table 1. Please clarify how the values in the last column of Table 1 are computed, and reconcile that calculation with the interpretation of Fig. 3A.

3. In the fits to experimental relaxation data, stretching exponents carry the key information on the extent of dynamic heterogeneity. Dynamic heterogeneity is central to the mechanistic interpretation, yet the manuscript does not provide a systematic analysis of these exponents across polymers and thicknesses. Please include such an analysis and clarify whether trends in the exponents support the trends hypothesized by the authors.

4. The extreme aspect ratio used in the “slender” simulation model could introduce artifacts. The manuscript should show that the conclusions are robust to system size and geometry. For example, do the authors still observe that horizontal displacements in the xy plane significantly exceed displacements in z for more isotropic (e.g., cubic) systems? Even a small set of checks would substantially strengthen confidence in the simulation-based claims.

5. At present, I do not see clear simulation-based evidence that links layer thickness to dynamic heterogeneity, or why the enhanced-motility layer can be thick (in the order of micrometers).

6. A higher Poisson ratio does not imply a material is “easier to shear.” Shear response is quantified by shear modulus. Please revise the discussion to use precise mechanical language and avoid incorrect implications.

7. The paragraph in lines 384–395 reads as highly speculative. Please separate what is directly supported by data from what is hypothesized.

Minor comments:

1. Fig. 1C would be clearer with h on the y-axis (consistent with the schematic in Fig. 3B).

2. Fig. 4A uses both color and symbol shape to encode the same label. Consider using symbol shape for ratios of relaxation times and color for polymers (or the other way around).

3. Normalizing Fig. 4B by PVC values does not seem necessary and may actually obscure both the fragility range and the length scale of the surface layer.

4. Consider adding an early schematic defining all relaxation times and thickness parameters in the conceptual model (τ_0, τ_1, τ_2, τ_{surf}, etc.). As currently presented, I had to go back multiple times while reading the manuscript to remind myself what each quantity meant.

5. Table 1 reports surface-layer thickness on page 6 but discussion on its last two columns appears much later (page 11). Consider splitting relaxation times and thickness values into separate tables to improve readability.

6. The “guide for the eye” in Fig. 7A seems to add very little. A simple linear fit would be less arbitrary (with the caveat that the dataset is only three points).

7. Labels for the different polymers with arrows are confusing and I don’t think are needed in Fig. 7B. You could use just different symbol shapes to improve readability. Also, open symbols would help to visualize instances where overlap exists.

8. The style of the scatter points in multiple figures (e.g., Fig. 1B, 4B, 7B) obscures data and is inconsistent with that on other figures (e.g., 1A, 2B, etc.). Consider a uniform, simpler plotting style.

Reviewer #3

(Remarks to the Author)
Nie and coworkers report a combined experimental and simulation manuscript to address the open problem of interfacial length scales related to the enhanced mobility of glassy (thin) films.
Using dynamic mechanical analysis on several glassy polymers of increasing fragility, they convincingly show that the existence and depth of two surface layers, one at the nanoscale and one in the micron range, strongly correlate with glass fragility.
Indeed, while the authors build on their previous work where this two-layer model was already established for specific polymers, the novel contribution of this work is the strong connection between relaxation times and length scales with fragilty, which is an important design parameter for material applications.

CG simulations in support of the experiments are also well constructed, and enough detailed are reported to replicate the work. While the "limited" simulation size (compared to experiments, though the simulations are quite large compared to the state of the art in the field) cannot directly probe the micron-size scale, velocity profile and displacement calculations at smaller scales (~50-100nm) are strong indicator of the larger-scale enhanced mobility observed experimentally, and the correlation with fragility holds consistently, where possible, between simulations and experiments.

I thoroughly enjoyed reading this manuscript and, without any major qualm, I recommend it for publication.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
The authors have modified the text following my remarks. The revised version of the text is suitable for publication.

(Remarks on code availability)

Reviewer #2

(Remarks to the Author)
The authors have addressed my comments, and I can now recommend the article for publication.

(Remarks on code availability)

Reviewer #1

Comment 1.0: *This manuscript by Nie et al investigates the connection between surface-induced mobility enhancement and intrinsic fragility in polymer glasses. Using stress relaxation experiments on a series of polymers spanning a broad range of fragilities, the authors show that both the nanoscale mobile layer thickness (h_t^nano) and the microscale propagation length (h_t) increase monotonically with bulk fragility. Complementary coarse-grained molecular dynamics simulations qualitatively reproduce the experimental trends and suggest that enhanced surface mobility propagates into the bulk via shear-like excitation modes whose penetration depth depends on fragility. The combination of macroscopic mechanical measurements and simulations is a strong aspect of the study, and the correlation between fragility and propagation length is intriguing and potentially impactful. Overall, the manuscript is of high interest for the glass and polymer physics community, so I strongly recommend considering for publication, after revision. The following comments are intended to further clarify and strengthen the presentation and interpretation.*

Response 1.0: We thank the reviewer for their effort reviewing our manuscript and providing valuable feedback for improvements. We will address their questions one-by-one below.

Comment 1.1. *The analysis of thin film data relies on a simplified Heaviside-step model for the depth-dependent relaxation time τ(z). While this provides a convenient parametrization and yields good fits, the physical meaning of a sharp discontinuity in τ(z) deserves further discussion. First, the extracted values of h_t^nano and h_t depend directly on this assumption. It would be useful to comment on the robustness of the conclusions with respect to smoother profiles (e.g., tanh). A brief discussion clarifying that the monotonic correlation with fragility does not depend critically on the sharp step assumption would significantly strengthen the manuscript. Second, the use of single relaxation times and linear (arithmetic) averaging of τ(z) may be nontrivial in systems with broad distributions of relaxation times. Since fragility is intrinsically related to the breadth and temperature sensitivity of relaxation spectra, it is reasonable to ask whether a Heaviside profile could partly reflect representing a smoother log τ(z) gradient on a linear τ scale. In other words, is the apparent bilayer a physical discontinuity, or could it arise from viewing a continuous distribution in linear τ? In the latter case, what would be the upper bound on the intrinsic width of the transition region consistent with the data?*

Response 1.1. We thank the reviewer for this comment. Below, we address the key questions raised.

Justification for using a Heaviside-step model for <τ(*z*)> rather than a smoother profile:

Schweizer and Simmons[1] analyzed how the thickness (h) dependence of an averaged dynamic property, <Θ> (where <…> denotes the arithmetic average) reflects the property's depth profile Θ(z). Comparing their analysis (reproduced as Fig. R1a below) with our result (Fig. 1b, reproduced as Fig. R1b) shows that the observed <τ> versus h is best captured when τ(z) is represented as a Heaviside step function. Most notably, functional forms that vary more gradually with z cannot reproduce the abrupt change to a constant value observed when h falls below two times the surface nanolayer thickness (h_t^{nano}) (Fig. R1b).

For films thicker than 200 nm, we measured relaxation moduli (examples shown in Fig. 2a) and found the data are well described by double stretched-exponential fits that also assumes a step-

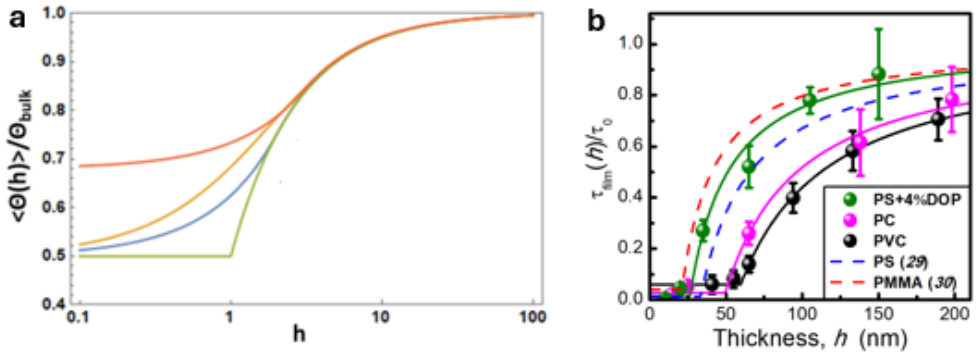

Fig. R1 **a** Predictions of normalized average dynamic property <Θ> versus log(thickness) for a step-function profile Θ(z) (green curve) and for profiles with more gradual gradients (curves of other colors). Adapted from Schweizer and Simmons[1]. **b** Experimental normalized average film relaxation time as a function of thickness (h) duplicated from Fig. 1b of the manuscript.

function profile for <τ> (solid lines, Fig. 2a). Although a gradual interfacial region between the fast and slow layers may be physically more realistic, introducing such a graded interface would require additional fitting parameters. We therefore adopt the step-function profile because it provides an adequate description with fewer parameters.

Sharpness of the actual τ(z) gradient:

Although our τ_{film} data is best described by a step-function, the actual τ(z) gradient could be much more gradual because we had determined τ_{film} by fitting our dynamic data to stretched-exponential functions, in which the relaxation time is characterized by a distribution of times rather than a single value. Therefore, the fitted values of τ_{film} and of the stretching exponent β indicate the distribution's average and width on the ln τ scale, respectively.

Figure R2a presents plots of fitted β values versus h for various polymers. As h increases from zero, β decreases continuously from ≈1 to a saturated bulk value of ≈0.4–0.7 at a characteristic thickness we label h_t^{nano} (Fig. R2a) and we attribute this behavior to a transition from the mobile surface nano-region to the slower region beneath. Fig. R2b shows that these h_t^{nano} values agree with those inferred from τ_{film} versus h in Fig. R1b, supporting our interpretation.

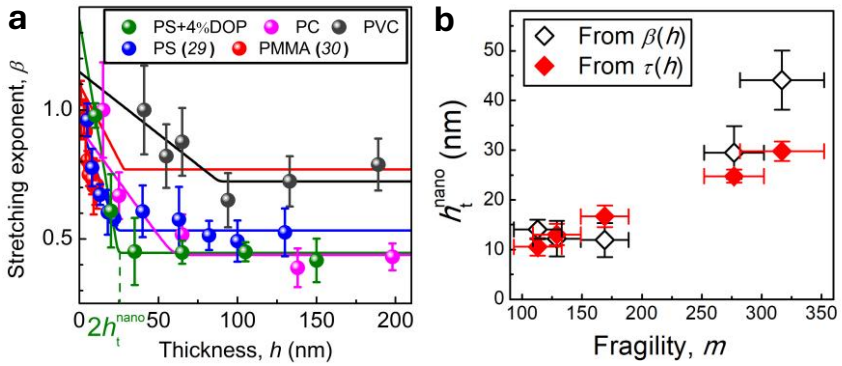

Fig. R2. a Stretching exponent β plotted versus film thickness h for various polymers. **b** Surface nanolayer thickness h_t^{nano} plotted against fragility m, with data coming from different sources: open diamonds are extracted from panel (**a**) as half the thickness at which β becomes independent of h; the red diamonds are obtained from Fig. R1b as half the thickness below which τ_{film} becomes constant.

These observations show that the relaxation time graduation evolves gradually with depth, even though the mean relaxation time exhibits a step-like profile. It has been demonstrated[2] that stretched-exponential relaxation corresponds to a distribution of energy barriers (or approximately $k_BT\ln(\tau/<\tau>)$ with an effective width on the order of k_BT/β with asymmetry towards low barriers. Such a distribution increases contributions of short-time (low-barrier) components to the average, which might explain why τ_{film} remains close to the accelerated near-surface value despite a gradually broadening spectrum with depth.

Justification for using arithmetic average:

In our analysis, $\tau(z)$ represents the local distribution of relaxation times at depth z, and the τ_{film} values we obtained from the stretched-exponential fits represent the average relaxation time $<\tau(h)>$ for the film-wide distribution. Because the film has a uniform cross-section at all z, this global average $<\tau(h)>$ is the arithmetic mean of the local mean values $<\tau(z)>$ taken across the whole film.

Summary:

Our answers to the key questions from the reviewer are: (1) the Heaviside-step model for $<\tau(z)>$ is appropriate because it fits the data better than broadened alternative profiles and describes the observations with the fewest fitting parameters. (2) Because the film has a uniform cross-section at all z, the global average $<\tau(h)>$, obtained from stretch-exponential fits, is the arithmetic mean of the local mean values $<\tau(z)>$ taken across the whole film. These support the validity of our model and analysis methods. (3) Although the local average $<\tau(z)>$ is well described by a step function, the underlying local $\tau(z)$ profile is in fact gradual, as indicated by the continuous variation of the stretching exponent β with depth.

We have added Figs. R2a, b to the Supplementary Information as Supplementary Figs. 2c, d, and added the above discussions to pp. 6-7.

Comment 1.2. *The identification of the fast mode (τ1) with the mobile surface region is well motivated and supported by the agreement between τ1 and τ0, as well as comparison with literature α-relaxation times . While their interpreation is physically-sound, the authors should avoid overinterpreting and consider that other relaxation modes (e.g., interfacial mechanical effects, heterogeneous stress distributions, beta or gamma relaxations, slow Arrhenius process) could also be involved.*

Response 1.2. We thank the reviewer's suggestion. Relaxation phenomena measured for the same system over the same temperature and time ranges are often interconnected. Accordingly, our observations may be related to other relaxation modes or mechanisms, such as mechanically mediated effects[3], slow Arrhenius process (SAP)[4], and free volume diffusion effects[5]. Investigating these possible connections would constitute a useful avenue for future study. We have added this point to p. 21 of the manuscript.

Comment 1.3. *A central finding of this manuscript is the correlation between the nanoscale mobile layer thickness and (reduced) fragility. While normalization of fragility values facilitates comparison between experiments and simulations, the physical meaning of a ratio of fragilities is not entirely straightforward. Since fragility is defined as the slope of log τ (and not linear τ, to reiterate on the previous comments) versus Tg/T at Tg, it is already a dimensionless measure of kinetic sensitivity. The*

authors should clarifying what additional physical insight is gained by plotting m normalized by that of PVC, and how the reader should interpret m/mPVC beyond simple rescaling.

In addition, the fragility values obtained in the coarse-grained simulations differ substantially in absolute magnitude from experimental values (in the SI, I read values around 20, which in real conditions are basically Arrhenius dependendes). Given this discrepancy, it may be too strong to imply that the simulated PVC quantitatively represents real PVC. It may be more precise to state that the simulations are performed on model polymer systems with systematically varied fragility, which reproduce the qualitative experimental trends. I think this change would actually add more "universality" to the claims (see limitations of this statement in the last comment).

Response 1.3. We thank the reviewer for raising the issue with Fig. 4b. We have clarified the figure as follows.

We thank the reviewer's comment. In this figure, both experimental and simulation data are presented. Because the simulations were performed at a higher temperature (1.35 T_g) than the experiments (T_g), the fragility values m from simulation are systematically smaller than those from experiment. The original figure, both datasets followed the linear relationship: h_t^{nano} = (constant) m. But combining them in one graph risked implying that normalized fragility has physical meaning. Therefore, we revised the figure so that the main panel now shows the experimental h_t^{nano} versus m, and the inset shows the simulated h_t^{nano} versus m. The figure caption is revised to indicate that $h_t^{nano} = A \cdot m$, where A = 0.093 ± 0.002 for the experimental data and A = 0.32 ± 0.01 for the simulated data. The main text describing Fig. 4b is also revised accordingly (see pp. 12 and 17). Figure R3 displays the updated version of Fig. 4.

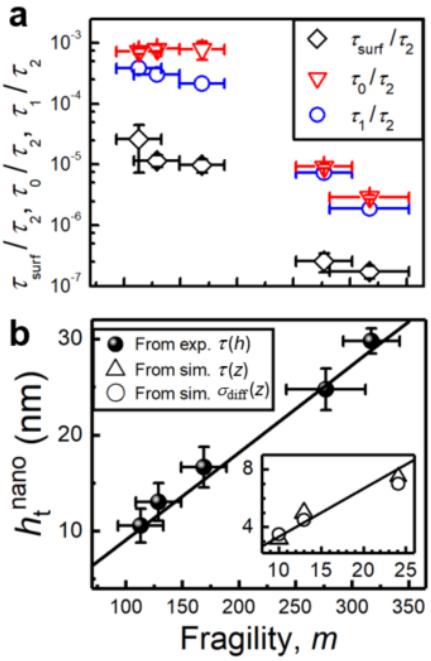

Fig. R3. The updated version of Fig. 4. In panel (**b**), the solid lines are the best fit lines, representing the relationship $h_t^{nano} = A \cdot m$, with A = 0.093 ± 0.002 in the main panel and A = 0.32 ± 0.01 in the inset. Panels (**a**) and (**b**) share the same horizontal axes.

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Comment 1.4. *The discussion interprets the propagation length ht primarily in terms of bulk fragility. However, previous work by the main author and by other groups (e.g., Polymer 51, 5309 (2010)) has*

shown that the fragility of surface layers can decrease relative to the bulk. This raises an interesting conceptual question: if the surface region is less fragile than the bulk, yet the present mechanism relies on bulk fragility to control long-range propagation, how are these observations reconciled? Is the shear-mediated propagation discussed here fundamentally governed by bulk dynamical properties, even if the local surface fragility differs? Or does the mechanism implicitly assume that the relevant "driver" is the surface-bulk dynamic contrast rather than absolute fragility values? A brief discussion clarifying whether in the view of the authors the process is mediated primarily by bulk dynamics, surface dynamics, or their contrast is needed.

Response 1.4. We thank the reviewer for this comment. Our results indicate that it is the bulk fragility of the polymer (m), rather than any local surface fragility, that determines the properties of the mobile surface layer. To emphasize this, we use "bulk" as an adjective for fragility: e.g., "the bulk fragility" in the Introduction (p. 3) and "the intrinsic fragility (m) of bulk linear polymer" in the Discussion (p. 19). For a discussion of how bulk fragility affects surface-induced mobility enhancement, please refer to the paragraph starting "Compared to strong glasses, …" on p. 20 of the manuscript.

Comment 1.5. *The manuscript presents fragility as a unifying parameter governing both nanoscale mobility enhancement and long-range propagation. Within the investigated systems, the monotonic correlation between h_t, h_t^nano and fragility is clearly demonstrated, and this is a strong point. However, the studied polymers are all linear systems with relatively narrow dispersity (at least for PS, upper limit of 2 for PVC) and without strong specific interactions.*
It would therefore be advisable to moderate the universality claims. Fragility often correlates with other material parameters that may also influence surface mobility propagation, such as chain stiffness, chemical architecture, cohesive energy density, Poisson's ratio, shear modulus, entanglement density, molecular weight, dispersity, ... Since these variables are not independently varied in the present dataset, fragility may partly act as a proxy for a broader set of structural and mechanical properties. Explicitly acknowledging that the framework has been validated for a specific class of linear polymer glasses, and that extension to branched, crosslinked, strongly associating, or network systems remains to be explored, would frame the conclusions more precisely without diminishing their impact.

Response 1.5. We thank the reviewer for this input. We have revised the discussion section on p. 19 and p. 20 of the manuscript to clarify that the materials investigated were linear polymers only and moderated the universality claim.

Reviewer #2

Comment 2.0. *In this work, the authors report a correlation between polymer glass-former fragility and the thickness of a near-surface layer with dynamics that differ from bulk behavior. The manuscript proposes a mechanistic picture in which increasing fragility leads to increased dynamic heterogeneity, which in turn sets the thickness of the anomalous surface layer. I have several comment I would encourage the authors to address before I can recommend this article for publication:*

Response 2.0. We thank Reviewer #2 for their time and careful reading of our manuscript and for the valuable comments. Below we address each point raised.

Comment 2.1. *1. The model used to fit the data in Fig. 1C already assumes a bilayer profile, so the bilayer structure is imposed by the fitting rather than emerging as a prediction from the data. In particular, the Heaviside-type transition seems to be part of the model rather than something uniquely supported by the measurements. Visualizing the data in Fig. 1C with a log-scale y-axis and providing a quantitative assessment of fit quality, especially for thinner films would be helpful.*

Response 2.1. We thank the reviewer for this comment. To address it, we adapt our Response 1.1 to Reviewer #1, which provides the following justification for modeling our τ vs. h data with a Heaviside step function: Schweizer and Simmons[1] analyzed how the thickness (h) dependence of an averaged dynamic property, $\langle\Theta\rangle$ (where $\langle\ldots\rangle$ denotes the arithmetic average), reflects the property's depth profile $\Theta(z)$. Comparing their analysis (Fig. R1a) with our result (Fig. 1b, reproduced as Fig. R1b) shows that the observed $\langle\tau\rangle$ versus h is best captured when $\tau(z)$ is represented as a Heaviside step function. Most notably, functional forms that vary more gradually with z cannot reproduce the abrupt change to a constant value observed when h falls below two times the surface nanolayer thickness (h_t^{nano}) (Fig. R1b).

Comment 2.2. *Fig. 3A appears to suggest that the thickness of the layer with enhanced-dynamics for PVC is approximately 724/2 nm (half of the film thickness at which bulk-like relaxation mode disappears). This seems inconsistent with the values reported in Table 1. Please clarify how the values in the last column of Table 1 are computed, and reconcile that calculation with the interpretation of Fig. 3A.*

Response 2.2. We thank the reviewer for this clarification. Figure 3a (previously Fig. 3A) indicates that $2h_t$ lies between 0.724 μm and 8 μm, i.e., 0.362 μm < h_t < 4 μm, which is consistent with the h_t = 2.51 μm reported for PVC in Table 1. The value of h_t was obtained as $h_t = h^*/2$, where h^* is the thickness at which the f_1 versus $1/h$ curve in Fig. 3c intersects $f_1 = 1$.

Comment 2.3. *In the fits to experimental relaxation data, stretching exponents carry the key information on the extent of dynamic heterogeneity. Dynamic heterogeneity is central to the mechanistic interpretation, yet the manuscript does not provide a systematic analysis of these exponents across polymers and thicknesses. Please include such an analysis and clarify whether trends in the exponents support the trends hypothesized by the authors.*

Response 2.3. We thank the reviewer for this important question. The stretching exponent (β) is an important parameter. We have plotted β versus h (Fig. R2a) and β_1, β_2 versus T (Figs. R4a, b), using analyses from the relaxation data.

In Fig. R2a, as h increases from zero, β decreases continuously from ≈1 to a saturated bulk-like value of ≈0.4–0.7 at a characteristic thickness that coincides with $2h_t^{nano}$ (independently determined from τ versus h; see Fig. R2b). This behavior supports the interpretation that near-surface dynamics are more liquid-like (local β value is closer to 1) and that a transition to bulk-like dynamics occurs as the film thickness exceeds h_t^{nano}.

In Fig. R4a, b, β_1 exceeds β_2. Furthermore, both β_1 and β_1 increase with temperature. These are consistent with the expectation that dynamics become less heterogeneous near the surface and with increasing temperature.

Figures R2a, b and Figs. R4a, b have been added to the Supplementary Information as Supplementary Figs. 2c, d and Supplementary Figs. 5a, b, respectively. Analyses of Fig. R2a have been added to p. 6 while those of Fig. R4a, b have been added to p. 9.

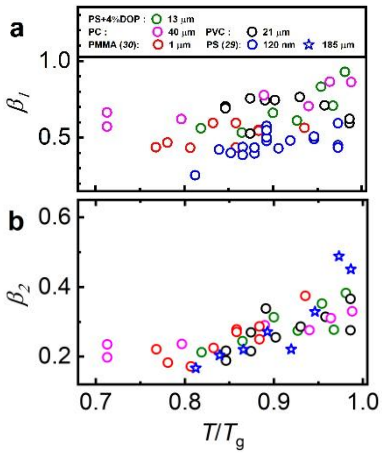


Fig. R4. Plots of β_1 (**a**) and β_2 (**b**) of the polymers studied as a function of temperature (T) normalized by the polymer's T_g. Reproduced from Supplementary Fig. 5.

Comment 2.4. *The extreme aspect ratio used in the "slender" simulation model could introduce artifacts. The manuscript should show that the conclusions are robust to system size and geometry. For example, do the authors still observe that horizontal displacements in the xy plane significantly exceed displacements in z for more isotropic (e.g., cubic) systems? Even a small set of checks would substantially strengthen confidence in the simulation-based claims.*

Response 2.4. We thank the reviewer for raising this issue. To address it, we constructed a new slender model that is identical to the original (Fig. 6a) except that L_x and L_y are doubled and L_z is halved. This doubles the number of monomers and reduces the aspect ratio L_z/L_x to 25% of the original model. Results of this model are presented in Fig. R5. As seen, they mirror the trends observed in Fig. 6a, strengthening the original slender model. We have added a discussion of this result to p. 15.

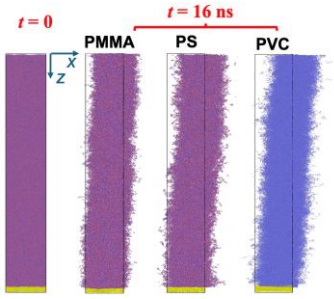


Fig. R5. The initial setup of the new slender CG model t = 0 (left), together with a side view along the y-axis showing the instantaneous atomic positions of PMMA, PS, and PVC molecules after t = 16 ns. After 16 ns, shear modes are developed in these models, with the strength of the shear mode being strongest for PVC, followed by PS and PMMA.

Comment 2.5. *At present, I do not see clear simulation-based evidence that links layer thickness to dynamic heterogeneity, or why the enhanced-motility layer can be thick (in the order of micrometers).*

Response 2.5. We thank the reviewer for this question. The primary simulation-based evidence linking the nanolayer thickness (h_t^{nano}) to dynamic heterogeneity (or fragility, m) appears in the inset of Fig. 4b (adapted as Fig. R6a below) which shows that the mobile nanolayer thickness h_t^{nano} increases with fragility, which is correlated with dynamic heterogeneity.

Simulations cannot directly measure the microscale mobile layer thickness (h_t) because the simulation box height is limited to 250 nm. However, they provide key supporting evidence (Figs. 6 and R5) for the existence of shear mode in the films, whose propagation distance (l) is identified to be the long-range mobile layer thickness (h_t), and underpin the mechanism for the observed long-range enhanced relaxation.

To strengthen the correspondence between the simulated and experimental layer thicknesses, we included a plot of simulated h_t^{nano} versus r.m.s. surface velocity (v_{rms}^{surf}) in Fig. 7b (adapted as Fig. R6b), which shows a clear proportional relationship between the two parameters. Notably, proportional relationships are also observed between the experimental h_t^{nano} and surface relaxation rate (τ_{surf}^{-1}), and between the experimental microscale surface layer thickness (h_t) and τ_{surf}^{-1} (Fig. 7c).

In our shear-mode picture, the lateral displacement (ξ) in the surface nanolayer initiates a long-range displacement field in the surface sublayer. Using the proportional relationships for h_t^{nano} and h_t noted above, l scales with ξ (Fig. R7a). However, our simulations use a box height smaller than l, so the shear-mode displacements are truncated by the rigid substrate, shown in Figs. R5 and 6a. Consequently, while simulations cannot demonstrate microscale h_t, they do establish a lower bound of 250 nm for h_t, which is longer than any existing theories can explain.

We have included an adaptation of Fig. R6b as Fig. 7b and the above discussion to pp. 17-19 and the figure caption of Supplementary Fig. 9.

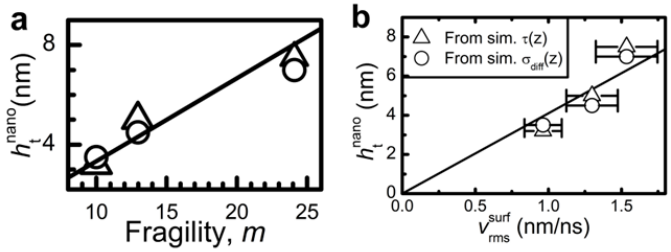


Fig. R6. Adapted from **a** Fig. 4 and **b** the newly added Fig. 7b in the manuscript. All solid lines are best linear fits.

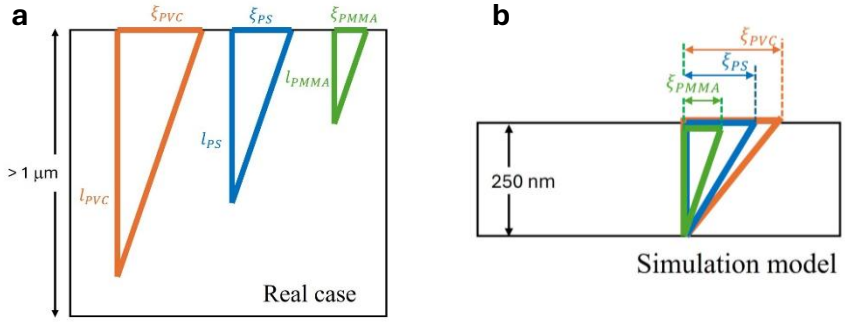


Fig. R7. Proposed displacement field in a shear excitation mode for different polymer models for **a,** thick films with $h > l$ and **b,** the simulation model with $h = 250$ nm ($< l$). This is reproduced from the original Supplementary Fig. 7. Note that this figure is now Supplementary Fig. 9, with panels **a** and **b** having been swapped.

Comment 2.6. *A higher Poisson ratio does not imply a material is "easier to shear." Shear response is quantified by shear modulus. Please revise the discussion to use precise mechanical language and avoid incorrect implications.*

Response 2.6. We thank the reviewer for raising this question. We have revised the text (on p. 20) as follows "Compared to strong glasses, fragile glasses exhibit a larger reduction in surface T_g relative to the bulk[6] and a sharper change in the temperature dependence of dynamic properties near T_g. Thus, the near-surface T_g gradient in fragile glasses is expected to produce a larger gradient in relaxation time or surface velocity enhancement. This effect may explain the greater surface-bulk dynamic contrast we observed in the more fragile polymer glasses."

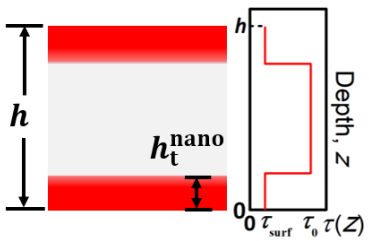
Comment 2.7. *The paragraph in lines 384–395 reads as highly speculative. Please separate what is directly supported by data from what is hypothesized.*

Response 2.7. We thank the reviewer for their comment and have revised the paragraph to the following with the changes marked in red: "Theoretically, our observations can also be interpreted within the potential energy landscape (PEL) framework, especially regarding its significant influence on the surface-enhanced dynamics [34]. Our results show that fragile polymers can support extensive propagation of surface-initiated fast displacements. This observation implies that the weaker structural connectivity—previously associated with fragile systems and linked in the literature to a more rugged PEL and higher dynamic heterogeneity [33]—facilitates the transmission of surface-initiated perturbations. In contrast, stronger glass formers, reported to have a relatively smooth PEL [33], which is consistent with easier random short-range exchange between neighboring atoms, resulting in a rapid spatial decay of shear energy. Taken together, these observations suggest that fragility may play a dual role: beyond its established use as a thermodynamic descriptor for the PEL, it could also serve as a structural predictor of an interface's ability to "drive" bulk dynamics. "

2.8. Minor comments:

Minor Comment 2.8.1. *Fig. 1C would be clearer with h on the y-axis (consistent with the schematic in Fig. 3B).*

Response 2.8.1. We thank Reviewer #2 for the suggestion and have revised Fig. 1c as shown below.



Minor Comment 2.8.2. *Fig. 4A uses both color and symbol shape to encode the same label. Consider using symbol shape for ratios of relaxation times and color for polymers (or the other way around).*

Response 2.8.2. We thank the reviewer for this comment. As the fragility values of the polymers are provided in Table 2, we decided that it is unnecessary to label them. Taking the reviewer's suggestion to improve clarity, we have revised Figs. 4a and 4b as shown below.

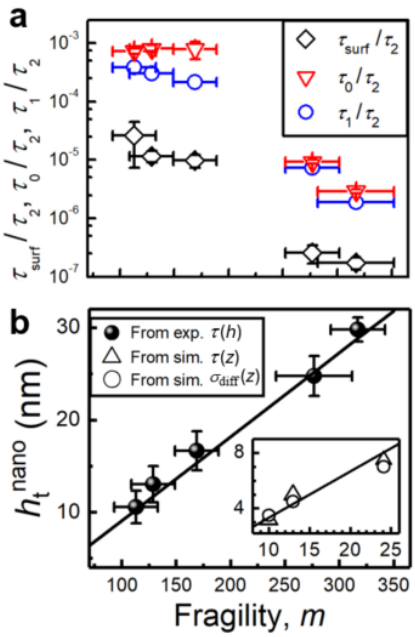


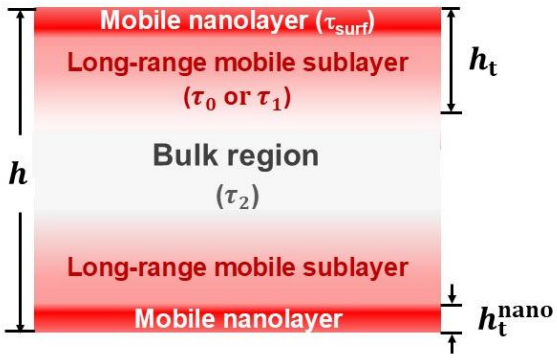
Fig. R8. Reproduction of the updated Figs. 4a and 4b.

Minor Comment 2.8.3. *Normalizing Fig. 4B by PVC values does not seem necessary and may actually obscure both the fragility range and the length scale of the surface layer.*

Response 2.8.3. We thank the reviewer for this comment and have revised Fig. 4b as shown in Fig. R8b.

Minor Comment 2.8.4. *Consider adding an early schematic defining all relaxation times and thickness parameters in the conceptual model (τ0, τ1, τ2, τsurf, etc.). As currently presented, I had to go back multiple times while reading the manuscript to remind myself what each quantity meant.*

Response 2.8.4. We thank the reviewer for this comment and have created a schematic as shown below and added it to the SI as Supplementary Fig. 1.



Minor Comment 2.8.5. *Table 1 reports surface-layer thickness on page 6 but discussion on its last two columns appears much later (page 11). Consider splitting relaxation times and thickness values into separate tables to improve readability.*

Response 2.8.5. We thank the reviewer for this suggestion. The manuscript currently has ten exhibits (8 figures and 2 tables), which has already reached the maximum number of exhibits allowed by *Nature Communications*. Therefore, we cannot create more.

Minor Comment 2.8.6. *The "guide for the eye" in Fig. 7A seems to add very little. A simple linear fit would be less arbitrary (with the caveat that the dataset is only three points).*

Response 2.8.6. We thank the reviewer for this comment. Although only three data points are available, the line shows that γ_σ is directly proportional to $v_{\mathrm{rms}}^{\mathrm{surf}}$, which is non-trivial. Furthermore, the line falls within the data error bar, providing visual support for this relationship. We have replaced the guided line with a fitted line and added information about the fit line in the figure caption: "The solid line is the best-fit line given by $\gamma_\sigma = (5.2 \pm 0.3\ \mathrm{s/m}) \times 10^{-3}\ v_{\mathrm{rms}}^{\mathrm{surf}}$."

Minor Comment 2.8.7. *Labels for the different polymers with arrows are confusing and I don't think are needed in Fig. 7B. You could use just different symbol shapes to improve readability. Also, open symbols would help to visualize instances where overlap exists.*

Response 2.8.7. We thank the reviewer for this comment and have revised Fig. 7b (which is currently Fig. 7c) as shown below. Information about the polymers is now provided in the figure caption: "**c** Plots of experimental h_t (left-axis) and $h_{\mathrm{t}}^{\mathrm{nano}}$ (right-axis) as a function of $\tau_{\mathrm{surf}}^{-1}/\tau_2^{-1}$, the relaxation rate contrast between surface and bulk, which increases in the order: PMMA < PS < PS + 4%DOP < PC < PVC.)

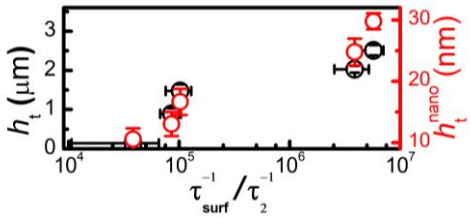


Fig. R9. Revised version of Fig. 7c.

Minor Comment 2.8.8. *The style of the scatter points in multiple figures (e.g., Fig. 1B, 4B, 7B) obscures data and is inconsistent with that on other figures (e.g., 1A, 2B, etc.). Consider a uniform, simpler plotting style.*

Response 2.8.8. We thank the reviewer for this comment. Because the comment is brief, it is difficult for us to identify the specific issues of the plots it refers to. However, we would like to mention that Figs. 1a, 2b, and 7b (currently Fig. 7c) cover a dynamic range spanning several orders of magnitude

and are therefore plotted on semi-logarithmic axes. In contrast, the dynamic range in Figs. 1b and 4b do not span such large ranges, so we retained linear-linear scales for those plots.

Reviewer #3

Comment 3.1: *Nie and coworkers report a combined experimental and simulation manuscript to address the open problem of interfacial length scales related to the enhanced mobility of glassy (thin) films.*

Using dynamic mechanical analysis on several glassy polymers of increasing fragility, they convincingly show that the existence and depth of two surface layers, one at the nanoscale and one in the micron range, strongly correlate with glass fragility.

Indeed, while the authors build on their previous work where this two-layer model was already established for specific polymers, the novel contribution of this work is the strong connection between relaxation times and length scales with fragilty, which is an important design parameter for material applications.

CG simulations in support of the experiments are also well constructed, and enough detailed are reported to replicate the work. While the "limited" simulation size (compared to experiments, though the simulations are quite large compared to the state of the art in the field) cannot directly probe the micron-size scale, velocity profile and displacement calculations at smaller scales (~50-100nm) are strong indicator of the larger-scale enhanced mobility observed experimentally, and the correlation with fragility holds consistently, where possible, between simulations and experiments.

I thoroughly enjoyed reading this manuscript and, without any major qualm, I recommend it for publication.

Response 3.1. We thank Reviewer #3 for their time reviewing our paper and support. Their comment precisely captures the essence and main contribution of this work.

References:

1. Schweizer KS, Simmons DS. Progress towards a phenomenological picture and theoretical understanding of glassy dynamics and vitrification near interfaces and under nanoconfinement. *J Chem Phys* **151**, 240901 (2019).
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4. White RP, Napolitano S, Lipson JEG. Mechanistic Picture for the Slow Arrhenius Process in Glass Forming Systems: The Collective Small Displacements Model. *Phys Rev Lett* **134**, 098203 (2025).
5. Boucher VM, Cangialosi D, Alegria A, Colmenero J. Enthalpy Recovery in Nanometer to Micrometer Thick Polystyrene Films. *Macromolecules* **45**, 5296-5306 (2012).
6. Ma Z, Nie H, Yan J, Tsui OKC. Correlation between fragility and surface glass transition temperature of polymers. *J Chem Phys* **159**, 224905 (2023).