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Invariant Fast Diffusion on the Surfaces of Ultra-stable and Aged Molecular Glasses

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Surface diffusion of molecular glasses is found to be orders of magnitude faster than the bulk diffusion, with a stronger dependence on the molecular size and intermolecular interactions. In this study, we investigate the effect of variations in bulk dynamics on the surface diffusion of molecular glasses. Using tobacco mosaic virus as probe particle, we measure the surface diffusion on glasses of the same composition but with orders of magnitude of variations in bulk relaxation dynamics, produced by physical vapor deposition, physical aging and liquid-quenching. The bulk fictive temperatures of these glasses span over 35 K, indicating 13 to 20 orders of magnitude changes in bulk relaxation times. However, the surface diffusion coefficients on these glasses are measured to be identical at two temperatures below bulk glass transition temperature T_g . These results suggest that surface diffusion has no dependence on the bulk relaxation dynamics when measured below T_g .

Molecular glasses have wide applications in electronics[1–3], coatings[4], pharmaceuticals[5–7], and nano-imprint lithography techniques[8]. Since the surface-to-volume ratio increases rapidly with the reduction in dimension as desired for these applications, understanding surface properties becomes increasingly important. Recent studies have aimed at developing efficient techniques to measure the surface mobilities on molecular glasses and have shown that surface diffusion can be orders of magnitude faster than bulk diffusion, with a lower activation barrier[9–13]. In addition, more recent studies reported that fast surface diffusion strongly depends on the molecular size and intermolecular interactions[12, 14, 15].

Understanding fast surface diffusion on molecular glasses is highly relevant for understanding the formation of ultra-stable glasses[16]. Organic glasses prepared by physical vapor deposition (PVD) at substrate temperatures below bulk glass transition temperature, T_g , are found to have exceptional thermodynamic and kinetic stabilities[16–19]. Glasses are out of equilibrium materials, therefore one can produce glasses with varying structures and properties by varying their states in the corresponding energy landscape. Physical aging is usually used to obtain glasses with varying properties by holding a glass below T_g . However, these changes in properties are typically small and take exponentially long times at lower temperatures. In contrast, within deposition time of minutes to hours, PVD can access states in the energy landscape that may take a liquid-quenched glass millions of years of aging to access[16, 19–21]. It has been proposed that due to the fast diffusion during PVD, molecules at the top surface have enough time to achieve a better configuration and thus a lower energy state before being buried by the next layer. Thus we call this process Surface-Mediated Equilibration (SME). Direct measurement of the surface diffusion on ultra-stable glasses is an important step in understanding the SME mechanism.

We have recently developed a new and efficient technique that uses tobacco mosaic virus (TMV) as probe

particle for facile characterization of surface diffusion on ordinary glasses[13]. When TMV is introduced onto the surface, due to rapid wetting a sharp curvature appears around the virus and induces surface molecules to flow towards it and form a meniscus. Since the virus is semi one-dimensional, the flow around the center of the virus has reduced dimensionality and is self-similar, allowing for rapid characterization of surface diffusion by tracking the evolution of the meniscus shapes. This technique requires no modification of the sample surface, as long as the aqueous TMV solution does not disturb its properties.

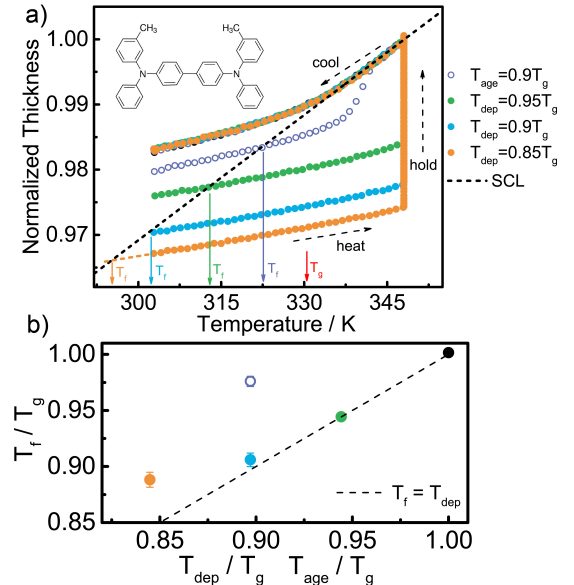


FIG. 1. a) Thermal stabilities of PVD and aged glasses post TMV measurements. Thickness changes of PVD glasses deposited at 0.85 T_g (solid orange), 0.9 T_g (solid blue), 0.95 T_g (solid green) and glasses aged at 0.9 T_g (open purple) were monitored upon heating and cooling with ellipsometry. Black dashed line is the universal super-cooled line for TPD. Arrows indicate the fictive temperature for each glass and bulk T_g . Inset shows TPD molecular structure. b) Fictive temperatures versus deposition or aging temperatures.

In this study, the TMV-probe method is applied on the surfaces of ultra-stable PVD glasses to investigate the effect of variations in bulk dynamics on the surface diffusion for the first time. Surface diffusions on glasses prepared by physical aging and liquid-quenching are also studied for comparison. The fictive temperatures of PVD stable, aged, and liquid-quenched glasses span over 35 K, corresponding to 13-20 orders of magnitude change in the bulk structural relaxation time, τ_α . Measurements are performed at two temperatures well below bulk T_g ($T_g - 27$ K and $T_g - 34$ K). We find that the surface diffusion coefficients of all these glasses at each temperature remain invariant within half an order of magnitude (range of experimental error). No correlation between the fast surface diffusion and the bulk relaxation dynamics was found, suggesting that the fast surface diffusion is possibly decoupled from bulk molecular motions and only reflect free surface behavior.

To produce glasses with varying bulk relaxation dynamics, N,N'-Bis(3-methylphenyl)-N,N'-diphenylbenzidine (TPD, $T_g = 330$ K) films were prepared either by PVD at various substrate temperatures, or by physical aging at $0.9 T_g$ for a week. Fictive temperature, T_f , is used as a measure of glass stability and bulk relaxation dynamics[22, 23]. Fig. 1 demonstrates how T_f was determined for each glass. Ellipsometry was used to measure the thickness of PVD or aged glasses as the films were heated at 10 K/min to 348 K and isothermally transformed into super-cooled liquid before being cooled back to glassy state at 10 K/min. Fig. 1a) shows the normalized thickness for each film during and after transformation (detailed in SI[24]). The excellent overlap in the super-cooled and ordinary glass states indicates that all glasses were transformed into a common super-cooled liquid state and had the same properties after transformation.

Fictive temperature is defined as the temperature where the extrapolated super-cooled liquid line intercepts the glassy line. Fig. 1a) shows the extrapolation of the super-cooled liquid line of TPD and the different temperatures where it intercepts with the initial glass lines. The T_f value of each glass is indicated by colored arrow. Fig. 1b) shows the measured T_f versus T_{dep} or T_{age} . Fig. 1 and Fig. S4[24] show that PVD glasses have lower fictive temperatures and higher stabilities compared to aged or liquid-quenched glasses, with the most stable glass deposited around $0.85 T_g$, consistent with previous studies of PVD glasses[16–19, 26–28].

The bulk τ_α of stable and aged glasses at a given temperature can be estimated based on Adam-Gibbs-Vogel (AGV) equation[29, 30]:

$$\ln \tau_\alpha(T, T_f) = \ln \tau_0 + \frac{DT_0}{T(1 - \frac{T_0}{T_f})} \quad (1)$$

where for TPD close to T_g , $D = 13.5$, $\tau_0 = 10^{-19.2}$ s,

$T_0 = 258.9$ K[28, 31]. One can estimate that for the most stable glass with $T_{dep} = 0.85 T_g$ ($T_f = 293$ K) τ_α is about 20 orders of magnitude slower than that of the liquid-quenched glass where $T_f = T_g = 330$ K for both isothermal hold temperatures of 296 K and 303 K (Fig. S6[24]). A more conservative Arrhenius extrapolation, using the activation energy near T_g , shows that τ_α for this sample is at least 13 orders of magnitude slower than τ_α at $T_g = 330$ K (Fig. S7[24]). As such, the range of bulk relaxation explored here spans 13 to 20 orders of magnitude, corresponding to 35 K changes in T_f .

TMV-probe experiments were performed to measure the surface diffusion of glasses with varying T_f values. This method has been described in detail in our earlier publication[13]. Briefly, the semi-one dimensional TMV particle is introduced onto the surface of a glass. Due to rapid wetting of the material, a sharp local curvature is produced around TMV, resulting in a flux of surface molecules towards the virus and forming a meniscus around it. Atomic force microscopy (AFM) is used to monitor the temporal evolution of the meniscus shapes. The unique advantage of using semi-one dimensional TMV probe, with a large aspect ratio around 18, is that it simplifies the meniscus evolution into a two-dimensional flow and thus simplifies the analysis needed to define the surface diffusion coefficient[13]. Control experiments were performed to rule out the potential effect of TMV deposition on stable glass properties in Fig. S5[24].

Fig. 2a) shows representative AFM images of a menis-

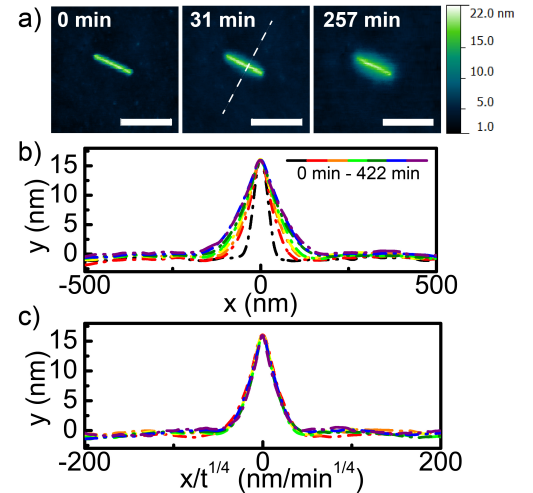


FIG. 2. a) Representative AFM images of the surface response to TMV perturbation on a 400 nm stable glass ($T_{dep}=0.85 T_g$) held isothermally at 303 K ($T_g - 27$ K). Scale bars are 400 nm. b) Temporal evolution of the profiles across the center of TMV shown in a), each profile plotted was averaged from five near-center line profiles across the TMV. c) Profiles in b) collapse onto a universal curve after scaling x with $t^{1/4}$, indicating that the profiles are self-similar and follow surface diffusion-controlled flow.

cus evolution formed after TMV was placed on the surface of a 400 nm stable glass film deposited at $0.85 T_g$, held isothermally at 303 K. The meniscus around the TMV probe, observed as bright halo in the image, is formed by material accumulation due to curvature driven surface flow, and grows with isothermal holding time. Since the aspect-ratio is large, the flow around the center of TMV is semi two-dimensional. A line profile normal to the long axis near the center of TMV, as the example shown in Fig. 2a), can be used to evaluate the evolution of the process shown in Fig. 2b). Five line profiles near the center of TMV were averaged to produce the profiles shown in Fig. 2b) at each given time for noise reduction. As seen in the plot, the cross-section profile widens with time as the sample is held at 303 K.

We note that in the time window of this measurement, no obvious embedding of TMV was observed, indicating that the meniscus formation is due to a diffusive process on the surface[13]. As demonstrated by Mullins[32], the governing equation for a flow solely driven by surface diffusion in two dimensions can be described as:

$$\frac{\partial h(x,t)}{\partial t} = -\frac{D_s \gamma \Omega^2 \nu}{kT} \frac{\partial^4 h(x,t)}{\partial x^4} \quad (2)$$

where $h(x,t)$ is the height at distance x from the center of TMV at time t , D_s is surface diffusion coefficient, γ is surface tension, Ω is molecular volume, ν is number of atoms per unit area, and k is the Boltzmann constant. Previous studies have shown that profiles following Eq. 2 are self-similar after a transient time[13, 32–35]. Fig. 2c) shows that the profiles in 2b) are indeed self-similar and collapse onto the same curve when x is scaled with $t^{1/4}$.

To further show that the meniscus evolution follows Eq. 2, the half profile widths at a constant height of 2 nm are plotted versus time in Fig. 3. For the temperatures and time intervals studied, all profile evolutions follow the $1/4$ power law scaling, further confirming that the flow of the molecules is governed by surface

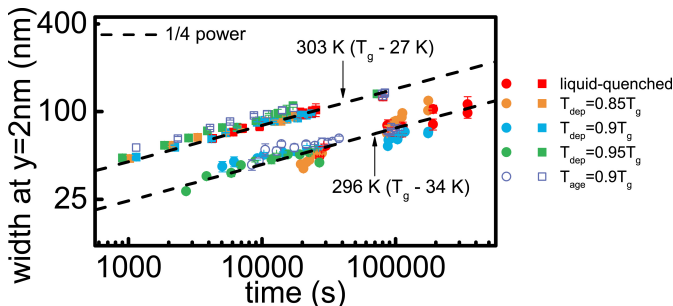


FIG. 3. Half profile widths at a constant height $h = 2$ nm from the bottom of TMV plotted versus isothermal hold times at 296 K and 303 K for five TPD glasses. At each temperature, the profile evolutions on different glasses all follow the $1/4$ power law indicated by black dashed lines.

diffusion. Under these conditions the prefactor $\frac{D_s \gamma \Omega^2 \nu}{kT}$ can be used to compare the value of surface diffusion for glasses with different bulk relaxation dynamics or fictive temperatures[13]. Except for D_s and T , other parameters in this prefactor depend on the molecule used and should be roughly the same for films of the same chemical composition (detailed discussions in SI[24]). It is interesting to observe from Fig. 3 that at each temperature, the profile width evolutions and therefore the prefactors are very similar for all five glasses surveyed. At each temperature, the data fall on the same line within the range of experimental error, suggesting that surface diffusion coefficients are the same for all of these glasses, decreasing with decreasing temperature.

With the data in Fig. 3, D_s for stable and aged glasses can be obtained by comparing the intercept value for each data set with that of liquid-quenched glass reported previously[13]. Fig. 4 plots D_s for each glass measured at two different temperatures as a function of T_f . The error bars represent variations between two to three independent measurements on newly deposited or aged samples. Fig. 4 shows that regardless of the preparation methods or T_f values, surface diffusion coefficients at each temperature remain the same within half an order of magnitude. The dashed lines show the average values of D_s at each temperature, where $D_s(303K) = (3.82 \pm 0.76) \times 10^{-18} \text{ m}^2/\text{s}$ and $D_s(296K) = (6.06 \pm 0.55) \times 10^{-19} \text{ m}^2/\text{s}$.

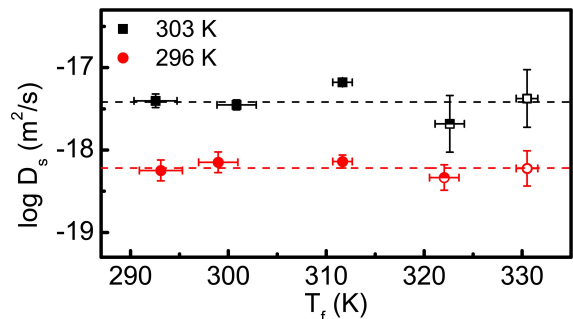


FIG. 4. Surface diffusion coefficients on stable (filled), aged (half filled) and liquid-quenched glasses (open) measured at 303 K (black) and 296 K (red), plotted versus fictive temperature. Dashed lines are the average D_s at each temperature.

The observation that surface diffusion is independent of bulk relaxation dynamics at each isothermal hold temperature is remarkable, given that the range of fictive temperatures spans over 35 K for the glasses surveyed. As discussed, this range of change in T_f translates into 13 to 20 orders of magnitude variations in τ_α between different glasses, with glasses deposited at $0.85 T_g$ having the slowest and liquid-quenched glasses having the fastest relaxation times. However, as shown in Fig. 4, even with such huge differences in bulk relaxation dynamics, the

measured surface diffusion coefficients on different glasses remain constant within experimental error.

Theoretical models based on smooth gradients of dynamics from the free surface predict temperature-dependent relaxation dynamics at the free surface with lower activation energy compared to bulk [36–40]. For example, models developed for equilibrium super-cooled liquids such as random first order transition (RFOT)[36] and coupling model (CM)[37] predict that for glasses with short range interactions, such as TPD, the surface relaxation time, τ_{surface} , has a power-law dependence on τ_{α} . In both models, τ_{surface} is predicted to be highly correlated with τ_{α} . To the best of our knowledge there are no predictions for out of equilibrium systems, and whether the surface dynamics would be coupled to the equilibrium state through the energy landscape, or would be coupled to out of equilibrium state due to dynamic coupling of molecules that are going through relaxation. The data presented here does not show any correlation between the bulk and surface dynamics, suggesting that as the system falls out of equilibrium there is a decoupling between the surface and bulk either due to the decoupling of the surface and bulk relaxation dynamics or the decoupling of the surface diffusion from surface relaxation dynamics (hopping). Since the Mullins model[32] that is developed for continuum fluid fits the data well, the latter is less likely. We also note that the data presented here does not rule out the coupling of the surface and the corresponding supercooled liquid, which is the same at each temperature despite fictive temperature variations.

Elastically cooperative activated barrier hopping model developed by Mirigian and Schweizer[41, 42] predicts surface diffusion as $D_s = d^2/(6\langle\tau_{\alpha}\rangle)$, where d is the molecular size and $\langle\tau_{\alpha}\rangle$ is the average dynamics of the near-surface layer at different penetration depths, either half or one molecular size[42]. Thus in this model D_s is only associated with the near-surface relaxation dynamics as opposed to bulk τ_{α} that strongly vary between stable, aged, and liquid-quenched glasses. Since one would not expect $\langle\tau_{\alpha}\rangle$ to change strongly within the depth of 1 nm or so from the free surface (approximately one molecular size), we can simply assume $D_s \simeq d^2/(6\tau_{\text{surface}})$. As such, from the invariance of D_s one could conclude that τ_{surface} is also invariant and is of the orders of $10^{-2} - 10^{-1}$ s assuming $d = 1$ nm. Such short time scales imply that the surface could be at equilibrium regardless of the bulk state. If this assumption is correct, then the surface relaxation times are not only orders of magnitude faster than bulk dynamics similar to what has been measured on polymer glasses[43], but they are also dynamically decoupled from the bulk dynamics such that a change of 20 orders of magnitude in the bulk relaxation times do not affect the surface relaxation times. Alternatively, the nature of the gradients in the dynamics in the layers immediately below the free surface could be different at various fictive temperatures, while

the free surface dynamics are determined by the nature of the interface and not the properties of the bulk. In either scenario, the origins of the temperature-dependence of τ_{surface} , measured through temperature-dependent D_s are not very clear and merit further exploration. Fig. 4 clearly shows that while D_s does not depend on T_f , it slows with decreasing temperature, consistent with previous measurements. It would be important to design experiments to independently observe the rotational dynamics of the free surface in order to directly measure τ_{surface} to verify this hypothesis.

Although less likely, it is still worth discussing the possibility that surface diffusion is due to a hopping mechanism of loosely bound surface molecules on an energy landscape produced by the out of equilibrium glassy solid[44, 45]. In this case fast diffusion can proceed even when the surface dynamics are also arrested and out of equilibrium. As glass densities have only changed by 1.5% between the most and least stable glasses (Fig. S4[24]), the surface energy has not been significantly varied (detailed in SI[24]). As such, it is plausible that the surface diffusion would also be independent of the fictive temperature. The activation energy for hopping in this scenario would only depend on the surface energy and molecular size.

The independence of D_s from the bulk relaxation dynamics is consistent with the proposed Surface-Mediated Equilibration (SME) process. The fact that D_s remains the same on glasses of various stabilities ensures that SME can proceed efficiently on the top surface layer regardless of the bulk dynamics. If the motion of molecules at the free surface slowed down significantly with the relaxation dynamics of previously formed layers, SME process would have been self-limiting and depends on film thickness, which is not the case[16, 19, 21]. However, the measurements presented here do not provide a full picture. Molecules of various sizes can be made into stable glasses when deposited at $0.85T_g$ [16, 19, 21]. This implies that τ_{surface} at $0.85T_g$ must be roughly the same for these molecules. Other studies have shown that D_s slows with increasing molecular size[12, 14, 15]. These two observations can only be simultaneously correct if D_s scales with molecular size as d^2 as predicted by Mirigian and Schweizer[41, 42], to keep τ_{surface} size invariant or if τ_{surface} and D_s are decoupled. One can verify the former hypothesis by performing surface diffusion measurements on a homologous series of molecules with various sizes. The latter can only be verified by directly measuring τ_{surface} .

In summary, we report the first measurement of surface diffusion on ultra-stable glasses, and compare with physically-aged and ordinary glasses. We find no change in the surface diffusion coefficients when the bulk fictive temperature is varied over a range of 35 K, equivalent to 13-20 orders of magnitude in bulk structural relaxation times. Our results suggest that fast surface diffusion is

decoupled from the bulk dynamics and is probably only associated with the near-surface dynamics that involve at most a few mono-layers of top surface molecules where they can always equilibrate at short time scales regardless of the bulk relaxations. However, the exact mechanism of this decoupling merits further investigation. Since surface diffusion can potentially contribute to fast crystallization and stable glass formation, a deeper understanding of the nature of fast diffusion and relaxation dynamics at the free surface are imperative for both glass theories and applications.

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