Surface diffusion is controlled by bulk fragility across all glass types

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Abstract. Surface diffusion is vastly higher than bulk mobility in some glasses, but only moderately enhanced in others. We show that this variation is closely linked to bulk fragility, a commonly used measure of how quickly dynamics is excited when a glass is heated to become a liquid. In fragile molecular glasses, surface diffusion can be a factor of 10^8 faster than bulk diffusion at the glass transition temperature, while in the strong system SiO_2, the enhancement is a factor of 10. Between these two extremes lie systems of intermediate fragility, including metallic glasses and amorphous selenium and silicon. This indicates that strong liquids resist dynamics excitation from bulk to surface and enables prediction of surface diffusion, surface crystallization, and formation of stable glasses by vapor deposition.

Glasses have liquid-like spatial uniformity and crystal-like mechanical strength, having countless applications from optics to electronics to drug delivery.[1,2,3] Recent work has highlighted the importance of surface mobility in the fabrication and stability of glasses. Utilizing high surface mobility,[4,5] crystal growth can be much faster on the free surface than in the bulk[6] and ultra-stable glasses can be prepared by vapor deposition.[7,8] In other areas, surface mobility impacts the stability of nanostructures, the resolution of nanolithography,[9,10] catalysis,[11] and particle sintering.[12] Because of this central role, understanding and predicting surface mobility is of strong interest.

Recent work has shown that surface diffusion can vary greatly across different glasses. For example, for molecular glasses at the glass transition temperature T_g, the ratio of surface to bulk diffusivity, D_s/D_v, can be as large as 10^8 and as small as 10^4, while the bulk diffusivity is approximately constant ($\sim10^{-20}$ m^2/s).[4,13,14,15] Simulations have observed similar effect for systems at higher mobility. For example, at $D_v = 10^{-12}$ m^2/s, $D_s/D_v = 1{,}000$ for the Kob-Andersen Lennard-Jones (KA LJ) mixture,[16] 20 for the metallic glass-former CuZr,[17,18] and 2 for the network system SiO_2.[19] There has been progress in the theory of surface mobility,[20,21,22] but the large variation across systems remains poorly understood.

We report that the large difference in surface diffusion between glasses is closely related to the fragility of bulk dynamics. Fragility is a widely used measure of the ease with which dynamics is excited when a glass is heated to become a liquid.[23] As Figure 1 shows, a strong system like SiO_2 resists such excitation; a fragile system like *o*-terphenyl (OTP) quickly gains mobility above T_g. The strong character of SiO_2 results from the robustness of its 3D network of covalent bonds, while the fragility of OTP results from the rapid unraveling of its local structure maintained by weak van der Waals interactions. Recently, Chen et al. reported a correlation between surface diffusivity and bulk fragility for a group of molecular glass-formers, with high surface mobility associated with high fragility.[24] Their work only covered the fragile extreme ,organic systems, and here we show that the conclusion holds for glasses across the entire fragile-strong spectrum, including chalcogenide, silicon, metallic, oxide systems, and computer glasses (KA LJ). Overall, these results now form the critical mass of evidence, leading to an important universal conclusion for all glass types consisting of various inter-particle forces.

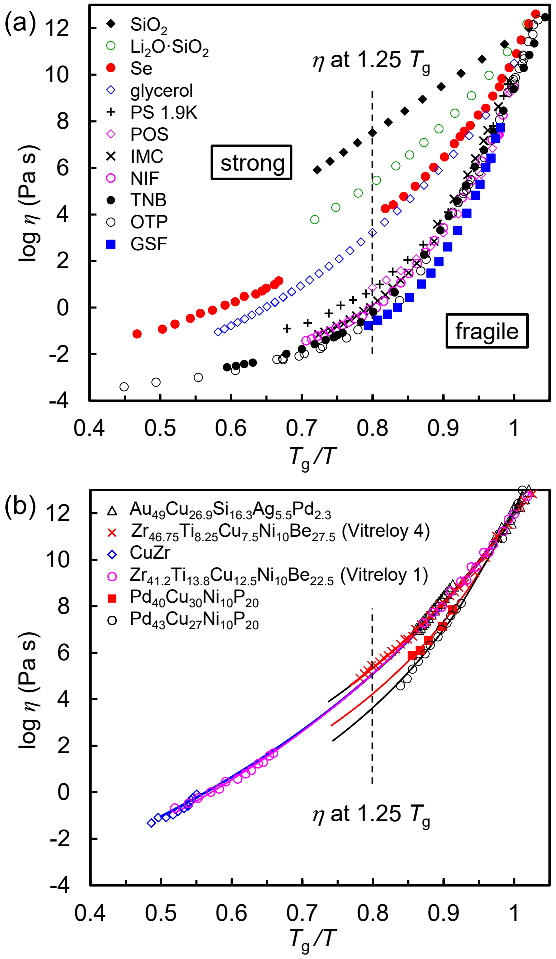

FIG 1. Angell plots of the viscosity of different materials. (a) Molecular liquids, selenium and oxides. (b) Glass-forming metallic liquids. See Table 1 for references.

Figure 1 shows the viscosity of the systems investigated here as functions of T_g scaled temperature (Angell plot). Metallic systems are plotted separately, in Figure 1(b), for clarity and for less complete data due to crystallization. In the Angell plot, the strong liquid SiO_2 shows Arrhenius behavior, whereas a fragile liquid such as OTP shows super-Arrhenius behavior. In this work, we use the viscosity at 1.25 T_g as the fragility measure (the vertical lines in Figure 1). While the concept of fragility is firmly rooted in glass science, its quantitative measure, using a single parameter, has not been standardized, with the current choices being m, D, $F_{1/2}$, and viscosity (or τ_α) at 1.25 T_g. While m is often used, as Richert and Angell point out, “it is disconcertingly unreliable due to author subjectivity in slope-taking at T_g as well as experimental subtleties in this slowly equilibrating regime”[25] For this reason we compare viscosity at 1.25 T_g where displacement from the Arrhenius behavior is large for better distinction of systems.For the systems studied, viscosity at 1.25 T_g spans 8 orders of magnitude (Table I). Molecular liquids lie at the fragile end with $\eta\,(1.25\ T_g) \approx 1$ Pa s, while SiO_2 resides at the strong end with $\eta\,(1.25\ T_g) \approx 10^7$ Pa s. In the middle, we find silicates, selenium, and metallic glasses, with $\eta\,(1.25\ T_g) \approx 10^5$ Pa s.

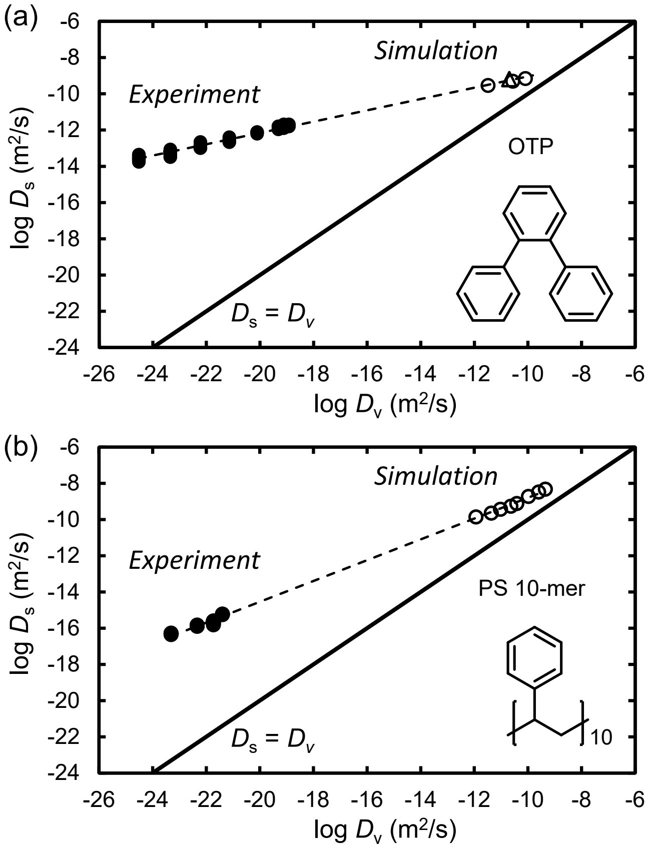

FIG 2. Power-law relation between surface and bulk diffusivity. (a) OTP. (b) PS 10-mer. For OTP, simulation results from this work (○, see the SI for details) and Ref. 34 (△). In each case, the dashed line is the power-law fitting of experimental and simulation results. The power law describes the relation between surface and bulk dynamics over a wide mobility range (15 decades in D_v).

Table I summarizes all the surface diffusion coefficients D_s of the glasses known at present. The D_s values are compared at the laboratory T_g, that is, at approximately the same bulk mobility. Over the past decade, D_s has been measured experimentally for various systems by following the evolution of surface contours driven by surface tension by our team and others.[4,13,14,15, 26 , 27 , 28 , 29 , 30 , 31 , 32 , 33] In addition, Table I includes D_s values from MD simulations for systems that have not been studied experimentally or are oversimplified for real systems. Because simulations were conducted at higher mobility than experiments, we extrapolate the results to the laboratory T_g for comparison with experimental values. For this, a power-law relation is applied between surface and bulk dynamics: $D_s \sim D_v^{\xi}$, where ξ is a constant between 0 and 1. This relation has been predicted by theories of surface mobility[20,21,22] and as shown in Figure 2, verified for systems for which both experimental and simulation results are available. For OTP (Figure 2(a)), experimental (solid circles)[13] and simulation (open symbols)[34] results connect smoothly by a straight line corresponding to the power law $D_s \propto D_v^{\xi}$ with $\xi = 0.32$. The same is true for polystyrene (PS) 10-mer (Figure 2(b)) for which experimental[15] and simulation[35] results follow the power law with $\xi = 0.57$. The larger ξ value for PS reflects a smaller mobility enhancement from bulk to surface relative to OTP.[15] For PS, we use the relaxation time τ from simulations[35] to calculate the diffusion coefficient: $D = d^2/(6\tau)$, where $d = 1.1$ nm is the size of the 10-mer.[21,36] For these systems, the power law provides an excellent description of the relation between D_s and D_v, over a wide range of mobility (15 decades in D_v). This result, along with its theoretical basis,[20,21,22] justifies our use of the power law to extrapolate simulation results to estimate D_s at the laboratory T_g (Figure S3). To our knowledge, this is the first test of the relation $D_s \propto D_v^{\xi}$ over a large mobility range accessed by experiments and simulations. The validation of the relation opens a new avenue to estimate dynamic properties at laboratory timescales from simulations.

Table I. Surface and bulk diffusion coefficients of glasses.

Systems	T_g, K	log D_s (m^2/s) at T_g	log D_v (m^2/s) at T_g	log η (Pa s) at 1.25 T_g	Method (ref.)
Kob-Anderson LJ	-	-11.5	-	-0.8	D_s (MD,16,37), η (MD,38)
Ortho-terphenyl (OTP)	246	-11.9	-19.5	-0.5	D_s (surface grating, 13; MD, 34, this work (see SI)), D_v & η (39)
Griseofulvin (GSF)	361	-12.4	-	-0.6	D_s (surface grating, 26)
Tris-naphthyl benzene (TNB)	347	-13.3	-20.2	-0.3	D_s (surface grating, 27), D_v & η (40)
Nifedipine (NIF)	315	-13.7	-	-0.1	D_s (surface grating, 28)
Indomethacin (IMC)	315	-14.0	-19.8	0.1	D_s (surface grating, 4), D_v (41)
PS 1.1k	307	-15.3	-	0.6	D_s (surface grating, 15)
PS 1.7k	319	-16.0	-	0.8	D_s (surface grating, 15)
PS 1.9k	332	-	-20.8	0.8	D_v & η (42)
PS 2.4k	337	-16.0	-	0.9	D_s (surface roughening, 33)
PS 3k	343	-16.3	-	1.0	D_s (surface step, 32)
Posaconazole (POS)	331	-16.8	-	0.9	D_s (surface grating, 14)
Se	308	-16.1	-	3.6	D_s (nano-hole filling, 31), η (43)
Si	843[a]	-16.7	-21.5	4	D_s (surface groove near crystal, 44, 45), D_v (46)
$Pd_{40}Cu_{30}Ni_{10}P_{20}$	566	-15.9 (519 K)[c]	-	4.2	D_s (surface grating, 29), η (47)
$Pd_{43}Cu_{27}Ni_{10}P_{20}$	580	-	-21.5	3.8	D_v (48), η (49)
$Au_{60}Cu_{15.5}Ag_{7.5}Si_{17}$	358	-17.1	-	5.3[b]	D_s (surface grating, 30), η (50)
CuZr	673	-16.9, -17.2	-	5.1	D_s (MD, 17, 18), η (51)
$Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ (Vitreloy 4)	622	-	-21.9	5.3	D_v (52), η (53)
SiO_2	1480	-20.7 (Si)	-21.9 (Si)	7.4	D_s (MD, 19, this work (see SI)), D_v (54), η (55)

[a] T_g obtained from Monte Carlo simulation (Ref. 56)
[b] Taken to be the same as the value for $Au_{49}Cu_{26.9}Ag_{5.5}Si_{16.3}Pd_{2.3}$ (Ref. 50)
[c] Obtained at 519 K, which is T_g - 47 K

In Figure 3, we plot the D_s and D_v values at T_g against the fragility of the bulk liquid. The D_s values exhibit a large variation, spanning 10 orders of magnitude for the systems investigated. We observe a strong correlation between D_s and fragility. The most fragile systems show a large enhancement of diffusion from the bulk to the free surface, by a factor of 10^8 for OTP. Within the molecular glasses, D_s decreases as the system becomes less fragile (stronger). SiO_2, the strongest liquid, shows a much smaller surface diffusion enhancement, by a factor of 10. Between these two extremes lie the systems of intermediate fragility: selenium, silicon, and metallic glasses. These systems show significant surface diffusion, but the enhancement factors are smaller than those for the molecular glasses. The overall trend is that higher surface diffusivity is associated with higher fragility. In contrast to the large variation of D_s, the D_v values show relatively small difference across systems, averaging around 10^{-21} m^2/s for all glass types. This weak dependence of D_v on fragility arises from the facts that (1) viscosity at the calorimetric T_g, used here to normalize temperature, increases slightly with decreasing fragility (see Ref. 57 and Figure S5), leading to lower D_v assuming validity of the Stokes-Einstein (SE) relation, and (2) the SE relation breaks down to a greater extent near T_g in fragile systems, causing an apparent enhancement of diffusion.[58]

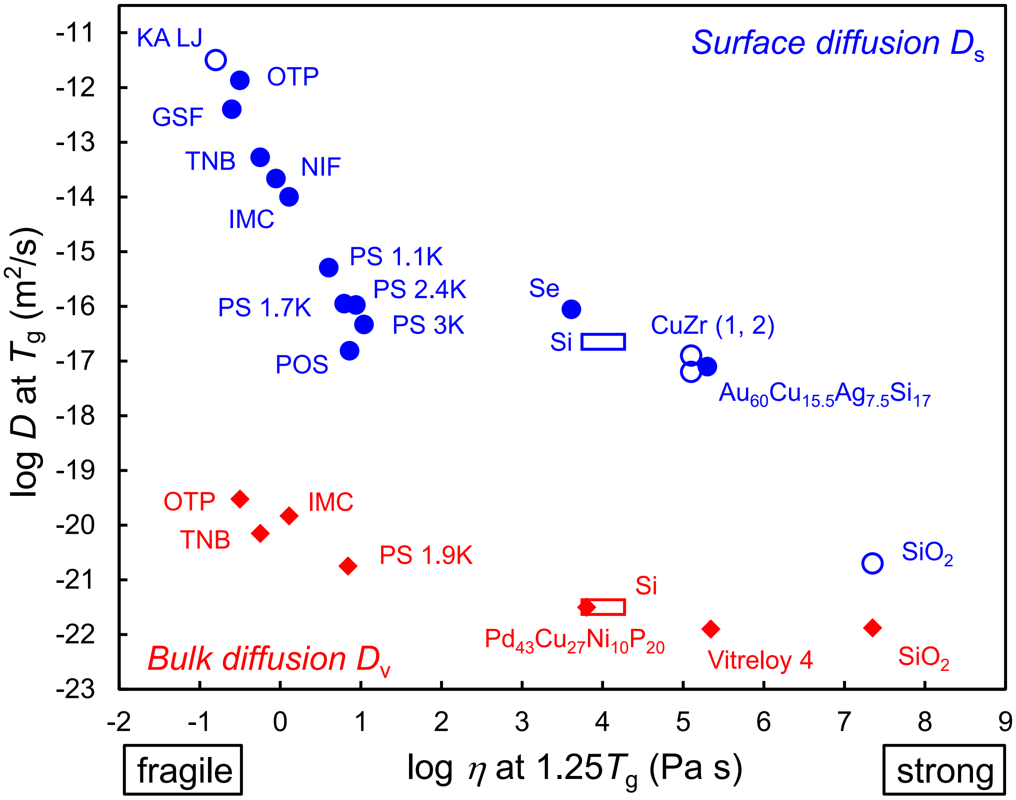

FIG 3. Correlation between diffusivity in glasses (D_s and D_v) and bulk fragility. For D_s, solid circles are experimental results and open circles are simulation results. All D_v values are experimental results. See Table 1 for data sources. For a-Si (open rectangles), the viscosity value is less certain due to a strong to fragile transition (see Ref. 60 and Figure S4).

The Figure 3 comparison includes two systems that deserve special comments. KA LJ is a simple model for fragile glass-forming liquids,[59] and according to Royall et al.,[38] has a similar fragility as OTP with $\eta\,(1.25\,T_g) = 0.2$ Pa s. This system has the highest D_s value in Figure 3 at the laboratory T_g (based on extrapolation discussed earlier, Figure S3). For amorphous silicon, a strong to fragile transition is proposed[60]and its viscosity at 1.25 T_g is estimated by interpolating the best available data (Figure S4). The estimated value (10^4 Pa s) is comparable to that of amorphous selenium.

Why is surface diffusion related to bulk fragility? By definition, strong systems have high resistance to thermal excitation around T_g. In the case of SiO_2, this high resistance results from the robustness of the strong network bonds between atoms. These bonds are largely intact as a glass is heated to become a liquid, leading to an Arrhenius dependence of viscosity on temperature. In contrast, fragile systems are composed of molecules that interact through non-directional van der Waals forces to form closely packed structures. Upon heating above T_g, the viscosity of a fragile system decreases sharply in a super Arrhenius manner, indicating a dramatic unraveling of the local bonding environment. The change of local environment from bulk to surface can also be regarded as a type of excitation (density reduction), analogous to thermal excitation. The local structure of a strong system is expected to be more resistant against this excitation, leading to a smaller increase of mobility. For SiO_2, simulations have found that the local environment of Si is largely unchanged from the bulk to the surface: in both environments, each Si is bonded to approximately 4 O atoms.[19] This stems from the robustness of the covalent Si-O bonds. Surface atoms reorganize themselves and preserve the low-energy tetrahedral bonding. Thus, in SiO_2, the diffusion of a Si atom faces essentially the same kinetic barrier, no matter whether it is in the bulk or on the surface. The picture is very different for a fragile van der Waals system. Simulations have shown a significant loss of nearest neighbors, by approximately 40 %,[61] when a bulk particle is transferred to the surface. For metallic systems, simulations have observed similar loss of nearest neighbors from bulk to surface.[17,18] This translates to a weakening of the caging effect that restricts motion and to a large surface enhancement of diffusion.[20,21] For a polymer in a surface layer, the different segments have different, depth-dependent environment and mobility.[62] The lateral diffusion rate of the whole chain is controlled by the deepest, slowest-moving segments. With increase of MW, D_s decreases, as seen in Figure 3 for the MW range 1 – 3 kg/mole and shown by Chai et al. up to 22 kg/mole.[63] Meanwhile, fragility decreases with increase of MW according to our fragility measure (log η at 1.25 T_g).[64] Thus, we expect the trend for PS in Fig. 2 to continue to higher MW. For amorphous silicon, simulations have also shown a significant change of structure from bulk to surface; for example, most atoms are four-coordinated in the bulk but many are three-coordinated on the surface,[65] leading to enhanced surface diffusion.[44,45]

The systematic trend in Figure 3 provides a foundation to predict the surface diffusion of amorphous materials and the transformations enabled by surface dynamics. Given that fast surface crystal growth is supported by fast surface diffusion,[26,31] we expect the phenomenon to be more significant in fragile glass-formers. Indeed, fast surface crystal growth is prevalent among molecular glasses,[26] but is less pronounced in stronger systems (e.g., a Pd-based metallic glass,[29] Se,[31] Si,[66] and silicates[67,68]). Similarly, given the importance of surface mobility in preparing ultra-stable glasses by vapor deposition,[7,8] we expect stable-glass formation to be a phenomenon that is more pronounced in fragile systems and less so in strong systems. This expectation is consistent with the correlation observed within molecular systems between the stability of vapor-deposited glasses and fragility.[69] For this group of molecules, the decrease of fragility is associated with the introduction of directional hydrogen bonds. Stable-glass formation has been reported for Se,[70] Si,[71] and metallic systems,[72] while the degree of stability enhancement appeared to be less than that observed for fragile organic systems.[70,72] In the case of SiO_2, vapor deposition typically produces high-energy, low-density structures relative to glasses prepared by liquid cooling.[73,74] Though further work is needed, the available literature is consistent with the notion that fragility influences the stability of vapor-deposited glasses.

In summary, our survey of all the available literature finds that the surface diffusion rate in glasses strongly depends on the fragility of bulk dynamics. This trend extends through all glass types: molecular, polymeric, chalcogenide, silicon, metallic, and oxide. The correlation is attributed to the robustness of covalent network bonds present in strong liquids, making them more resistant to environmental excitation from bulk to surface. At present, the surface diffusion data are more extensive on molecular glasses than on other glass types. Further work is warranted to learn whether a similar trend exists within each glass type, with the metallic glasses being a potentially fruitful target.[18] This finding helps understand and predict surface mobility to develop amorphous materials with high stability for their diverse applications.

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Supporting Information. Surface and bulk diffusion by simulations (OTP and silica), extrapolation of surface diffusivity from simulations to laboratory T_g, viscosity of silicon, and viscosity at calorimetric T_g plotted against fragility.

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