

Surface-Mediated Formation of Stable Glasses

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Annu. Rev. Phys. Chem. 2023. 74:361–89

First published as a Review in Advance on
February 7, 2023

The *Annual Review of Physical Chemistry* is online at
physchem.annualreviews.org

<https://doi.org/10.1146/annurev-physchem-042018-052708>

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Keywords

stable glass, physical vapor deposition, surface-mediated equilibration, structural anisotropy, glass transition, enhanced surface mobility

Abstract

Surfaces mediate the formation of stable glasses (SGs) upon physical vapor deposition (PVD) for a wide range of glass formers. The thermodynamic and kinetic stability of SGs and their anisotropic packing structures are controlled through the deposition parameters (deposition temperature and rate) as well as the chemical structure and composition of the glass former. The resulting PVD glass properties can therefore be related to the structure and dynamics of the glass surface, which can have oriented packing, enhanced surface diffusion, and a lower glass transition temperature, and can facilitate an enhanced aging rate of the interfacial region. We review our current understanding of the details of this surface-mediated SG formation process and discuss key gaps in our knowledge of glass surface dynamics and their effect on this process.

PVD: physical vapor deposition

SG: stable glass

T_m : melting point

SCL: supercooled liquid

T_g : glass transition temperature

1. INTRODUCTION

Glasses are widely used in applications where large-scale homogeneous properties are desired. For example, high-refractive-index glass thin films are used as coatings on multilayer interferometer mirrors in gravitational-wave interferometric detectors, where low noise and high sensitivity are critical (1, 2). However, because of their nonequilibrium nature, glasses can evolve over time through physical aging, crystallization, and degradation, which can lead to undesired property changes. Glasses typically have higher energy and lower density than their crystalline counterparts, which also affect properties such as electric and thermal conductivity and mechanical performance. Recent studies have shown that stable glasses (SGs) produced through physical vapor deposition (PVD) can overcome many of these challenges (3–7), broadening their potential use in applications. These glasses have access to alternative structures and properties at their free surface, which can be preserved upon vapor deposition (8–16). While recent reviews have highlighted the unique properties of SGs (4–7), many details of their formation remains underexplored. In this review, we summarize our current understanding of the role of free surface structure and dynamics in surface-mediated SG formation.

2. STABLE VAPOR-DEPOSITED GLASSES

When a liquid is cooled below its melting point (T_m), the relaxation dynamics of the supercooled liquid (SCL) become too sluggish to maintain equilibrium (**Figure 1**), thus forming a glass at the glass transition temperature (T_g). Physical aging below T_g can allow a liquid-quenched glass

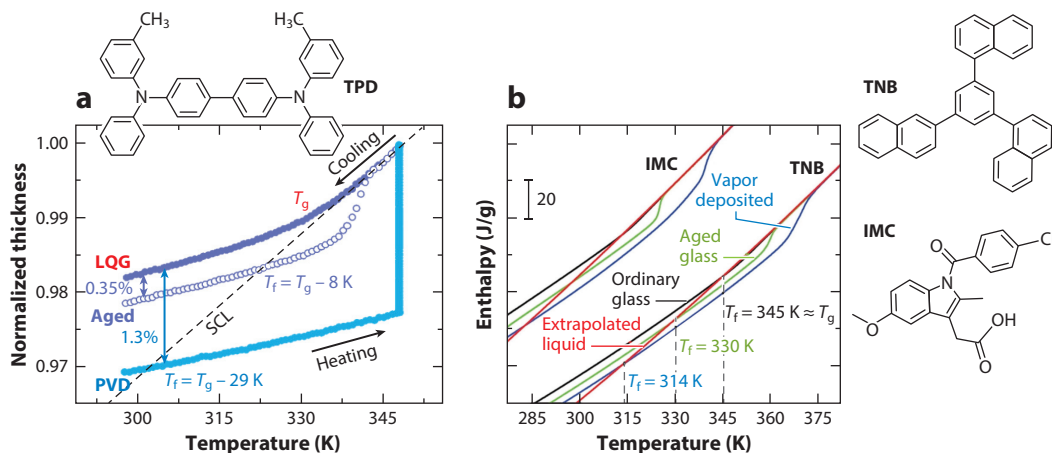


Figure 1

(a) Normalized thickness versus temperature of ~ 200 -nm films of TPD (structure shown above the graph) produced by physical aging at 298 K for 1 week (open purple circles) and by PVD at $T_{\text{dep}} = 298$ K (filled blue circles), measured using spectroscopic ellipsometry. Upon heating and subsequent cooling (black arrows), the corresponding LQ is produced at $T_g = 331 \pm 3$ K. In each film, T_f is measured as the intersection between the extrapolated SCL (dashed black line) and the heating curve, and $\Delta\rho$ is estimated on the basis of the relative change in thickness upon transformation. The PVD glass has a lower T_f and a higher density ($T_f = T_g - 29$ K; $\Delta\rho = 1.3\%$) than the aged glass ($T_f = T_g - 8$ K; $\Delta\rho = 0.35\%$). It takes $\sim 10^6$ – 10^9 years to produce an aged glass with equivalent corresponding properties. (b) Enthalpy versus temperature, calculated from heat capacity measurements, for TNB and IMC films (structures shown on the right), produced by PVD (blue), liquid cooling (black), and physical aging (green). The intersection of the extrapolated SCL line (red) and the glass line defines T_f for each film, as shown for TNB. Abbreviations: IMC, indomethacin; LQ, liquid-quenched glass; PVD, physical vapor deposition; SCL, supercooled liquid; TNB, 1,3-bis-(1-naphthyl)-5-(2-naphthyl)benzene; TPD, N, N'-bis-(3-methylphenyl)-N, N'-diphenylbenzidine. Panel a adapted with permission from Reference 23; copyright 2017 American Physical Society. Panel b adapted with permission from Reference 3; copyright 2007 American Association for the Advancement of Science.

(LQG) to equilibrate toward its corresponding SCL state (17). However, due to the increasing barriers for relaxation at low temperatures, physical aging can be prohibitively slow (18–20). This is because the activation energy for structural rearrangement (α relaxation) in SCLs increases upon cooling. The degree of this increase in activation energy is characterized by fragility (21), which can vary from ~ 16 for a strong liquid with Arrhenius relaxation behavior to ~ 190 for an extremely fragile glass whose activation energy increases dramatically upon cooling, thus showing non-Arrhenius temperature dependence. Many glasses also exhibit fast localized rearrangements below T_g (β relaxation), which precedes α relaxation (22). The thermodynamic and kinetic stability of glasses can be characterized upon heating, either through measurements of the fictive temperature (T_f) (**Figure 1**) or through measurements of relaxation dynamics upon heating to various temperatures (19).

In 2007, Swallen et al. (3) discovered that when organic molecules are vapor-deposited onto substrates held below T_g at slow deposition rates (R_{dep}), SGs are produced with extraordinary thermodynamic (10, 24, 25) and kinetic (26–28) stability and 1–1.5% higher density (10, 13, 29) in comparison to their LQG counterparts (for examples, see **Figure 1**). The degree of stability in SGs can be analogous to glasses aged for millions of years (3, 25). SGs also exhibit other superior properties, such as lower enthalpy (25), improved hardness and modulus (30–35), lower heat capacity (26), improved resistance to both surface (36) and bulk crystallization (37–39), suppressed low-energy excitations as measured through tunneling two-level systems (TLS) (40, 41), and suppressed β relaxation (42). For thin films of amorphous silicon (1, 43, 44) and germania glasses (2), deposition at a substrate temperature (T_{dep}) of $\sim 0.8T_g$ is more efficient than postgrowth annealing in modifying the glass microscopic structure and in reducing room-temperature internal friction and density of TLS, which are paramount for improving the sensitivity of next-generation interference coatings for gravitational-wave interferometer mirrors (1, 2). Rodríguez-Viejo and colleagues (45) have demonstrated that SGs of organic semiconductors can significantly improve the efficiency and lifetime of organic light-emitting diodes. SGs can be produced in a broad range of glass-forming systems, including molecular (4, 7), polymeric (46–48), metallic (32, 33, 37, 49), and chalcogenide glasses (38, 50), as well as in simulated Lennard–Jones systems (51, 52), covering a wide range of fragility from ~ 40 in metallic glasses (32, 33, 37) to ~ 140 in polymers (46–48) and from 56 to 149 in molecular glasses (53–56).

First observed through measurements of optical birefringence (13, 57), molecular orientation is also a general feature of PVD glasses deposited at low T_{dep} (5, 6, 8, 10, 57–59). Molecular anisotropy leads to other anisotropic properties such as heat flow propagation (60). PVD glasses also show packing anisotropies that indicate closer molecular distancing in the direction of deposition (i.e., molecular layering) (9, 14, 16, 61). Molecular layering also results in anisotropy in properties such as hardness and modulus (31, 35) and contributes to the value of optical birefringence (57, 61). These unique properties of SGs are not available in LQGs, indicating that PVD provides access to limiting deep states of the energy landscape (4). Access to these states is critical for probing the validity of various theoretical predictions for the existence of the ideal glass phase, which can prevent the Kauzmann entropy crisis (62), or other possible pathways by which this crisis can be avoided (63–65). Remarkably, Ediger and collaborators (66) have demonstrated that PVD glasses of ethylbenzene can be deposited in near-equilibrium states with T_f values within a few degrees Kelvin above the Kauzmann temperature (T_K). Another study in Teflon also achieved exceptionally low T_f values upon PVD (67). Moreover, previously unknown liquid crystalline phases have been produced in vapor-deposited molecules that are not otherwise liquid crystalline (68), and polyamorphic states have been achieved through deposition of amorphous selenium under light (50) and deposition of a molecular glass in the thin-film state (69), which are not realizable through liquid cooling.

LQG:

liquid-quenched glass

T_f : fictive temperature

R_{dep} : deposition rate

T_{dep} : deposition
substrate temperature

Kauzmann entropy

crisis: at T_K , the
extrapolated
configurational
entropy of SCL goes
to zero, which violates
the second law of
thermodynamics

T_K : Kauzmann
temperature

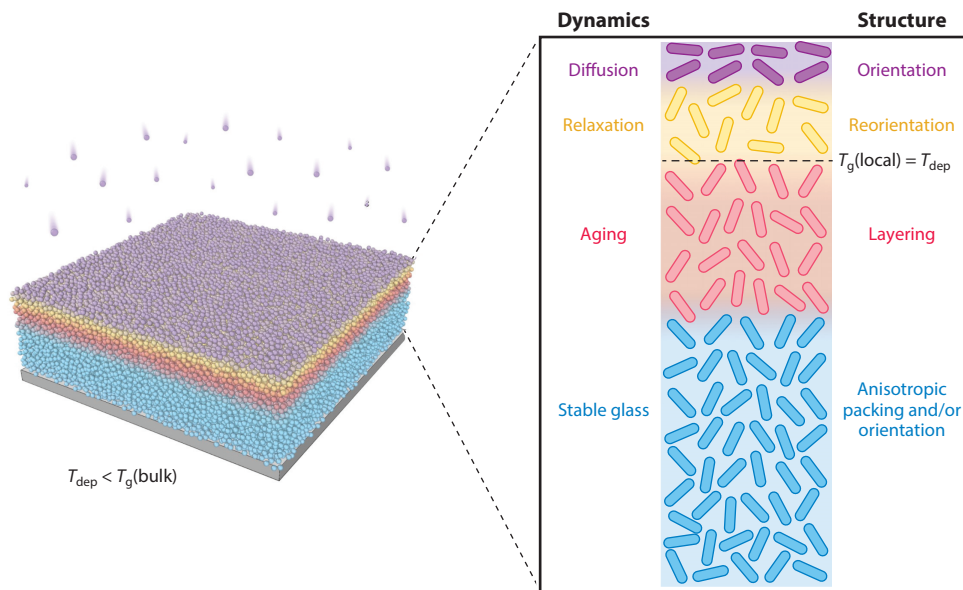


Figure 2

Schematic illustration of surface-mediated stable glass formation at $T_{\text{dep}} < T_g(\text{bulk})$. The lozenge shapes illustrate the preferred orientation of nonspheroidal molecules. The dashed line denotes the position where $T_g(\text{local}) = T_{\text{dep}}$. The film can be divided into four possible regions. At the topmost layer (*purple*), the free surface can impose molecular orientation, which is typically in-plane. Molecular mobility in this layer is dominated by lateral surface diffusion. Below the free surface (*yellow*), relaxation dynamics are enhanced and the layer reaches equilibrium at the timescale of deposition, $T_g(\text{local}) < T_{\text{dep}}$. Molecules can reorient into the equilibrium configuration of this layer, which can be either isotropic or oriented depending on the layer's thickness. Farther away from the free surface, where $T_g(\text{local}) > T_{\text{dep}}$ (*pink*), the liquid falls out of equilibrium but may have an accelerated aging rate compared with the bulk, leading to further equilibrium. Aging under the constraint imposed by the immobile layer below can result in tighter out-of-plane distancing (i.e., layering). Well below the surface (*blue*), the molecules are kinetically arrested at the structure and stability that are achieved by a combination of the properties gained in the three interfacial regions.

During PVD, fresh surfaces are successively produced by the incoming flux of material. When T_{dep} is held below T_g , the film's interior is arrested in an immobile state. However, close to the vapor–glass interface (i.e., the free surface), the relaxation dynamics are enhanced by orders of magnitude (23, 70–74), and the structure of the liquid is modified (51). By taking advantage of the enhanced surface mobility and its gradients, a growing PVD glass can explore more stable configurations and adopt unique structures that originate at the free surface. These properties can be tuned through chemical structure (16, 51, 75), deposition temperature (13, 24, 31), and deposition rate (14, 25, 27). While there is now extensive empirical knowledge about how to achieve stability upon PVD, many details of surface-mediated SG formation remain poorly understood. For example, while enhanced surface diffusion correlates strongly with SG formation, in some systems stability can emerge in the absence of enhanced surface diffusion (76). As illustrated in **Figure 2**, different interfacial regions can utilize different pathways toward stability. In this review, we provide direct and indirect evidence for the existence and properties of each of these regions and discuss their influence on the final structure and stability of a PVD glass under certain deposition conditions. This review focuses on molecular glasses, because they have been extensively studied (16, 75, 77), but we provide other examples when possible.

3. FACTORS CONTROLLING THE STRUCTURE AND PROPERTIES OF VAPOR-DEPOSITED GLASSES

Deposition temperature and rate are the two main factors that are predictably used to control stability, while molecular shape, intramolecular flexibility, and intermolecular interactions can affect structural details such as anisotropy. Light has also been utilized to alter the PVD glass structure (50). While an exhaustive review of these dependencies is outside the scope of this article, the subtle ways that each factor plays a role in the PVD glass structure and stability can elucidate the details of the various stages of surface-mediated SG formation (**Figure 2**).

T_{onset} :
onset of thermal
transformation upon
reheating

3.1. The Effect of Deposition Temperature and Deposition Rate

Deposition temperature is one of the key parameters in determining stability. In most systems, deposition just below T_g ($T_{\text{dep}} > 0.9T_g$) produces glasses with near-equilibrium properties analogous to the extrapolated SCL state. The most stable glasses, as measured either through density and T_f (thermodynamic stability) or through the onset of transformation above T_g (T_{onset} , kinetic stability), are typically produced in the range of $0.8T_g < T_{\text{dep}} < 0.9T_g$. Deposition at lower temperatures generally results in less stable glasses that have only partially “aged” toward the corresponding SCL state (24, 78, 79). Measurements of other properties such as optical birefringence (5, 10, 13) and mechanical performance (31, 35) also show nonmonotonic T_{dep} dependence of stability.

Figure 3 shows a recent example of research from our group that explores the T_{dep} dependence of properties for two structurally similar molecules, 9-[3,5-di(naphthalen-1-yl)phenyl]anthracene (α , α -A) and 9-[3,5-di(naphthalen-1-yl)phenyl]phenanthrene (α , α -Phen) (**Supplemental Table 1**) (16). The relative density change compared with the LQG ($\Delta\rho$), measured using spectroscopic ellipsometry (SE), is an indirect measure of thermodynamic stability, with a higher density corresponding to a lower T_f value (**Figure 1a**). Molecular layering (**Figure 3c**) is measured in grazing-incidence wide-angle X-ray scattering (GIWAXS) experiments as an anisotropic peak in the vertical (out-of-plane) direction at a distance of approximately the molecular size (14) (for α , α -A, see **Figure 3c, inset**). This anisotropic structure, which is erased upon annealing above T_g , has been observed in a wide range of PVD glasses (9, 14–16, 36, 40, 80, 81) and in simulations (12). The layering peak has been attributed to closer interparticle packing in the vertical direction (16, 61), and it contributes to the positive value of optical birefringence (16, 61), even in spherical molecules such as α , α -A (16, 61) (**Figure 3d**). Optical birefringence also arises from in-plane (negative) and out-of-plane (positive) molecular orientation in nonspherical molecules such as α , α -Phen (5, 9, 10, 13) (**Figure 3d**). As shown in **Figure 3**, all three quantities show nonmonotonic T_{dep} dependence, which can be broken down into three distinct regimes. At $0.93T_g < T_{\text{dep}} < T_g$ (340–365 K), the density follows the extrapolated SCL. SGs produced in this region are isotropic and show neither layering nor birefringence, indicating that near-equilibrium states have been achieved. As T_{dep} decreases, the density continues to increase, with a maximum at 300 K ($0.82T_g$), but it never reaches the corresponding SCL values, indicating partial equilibration. In this regime, layering and birefringence rapidly develop and increase with decreasing T_{dep} . At $T_{\text{dep}} \leq 300$ K, the density decreases with decreasing T_{dep} in a molecule-specific manner.

While the details of density's T_{dep} dependence can vary with molecular structure, its nonmonotonic behavior has been observed in a broad range of molecules (10, 13, 29, 59). Similar behavior is also observed in measurements of T_f (24, 28) and T_{onset} (26, 53, 81–83), where thermodynamic and kinetic stability are optimized around $0.85T_g$ in most systems. These trends are analogous to the nonmonotonic trends observed in physical aging for a constant length of time (84), but with estimated aging times of thousands to millions of years (23, 25, 29, 42). This means that the effective rate of equilibration at the free surface region can be enhanced by 10–15 decades compared

Supplemental Material >

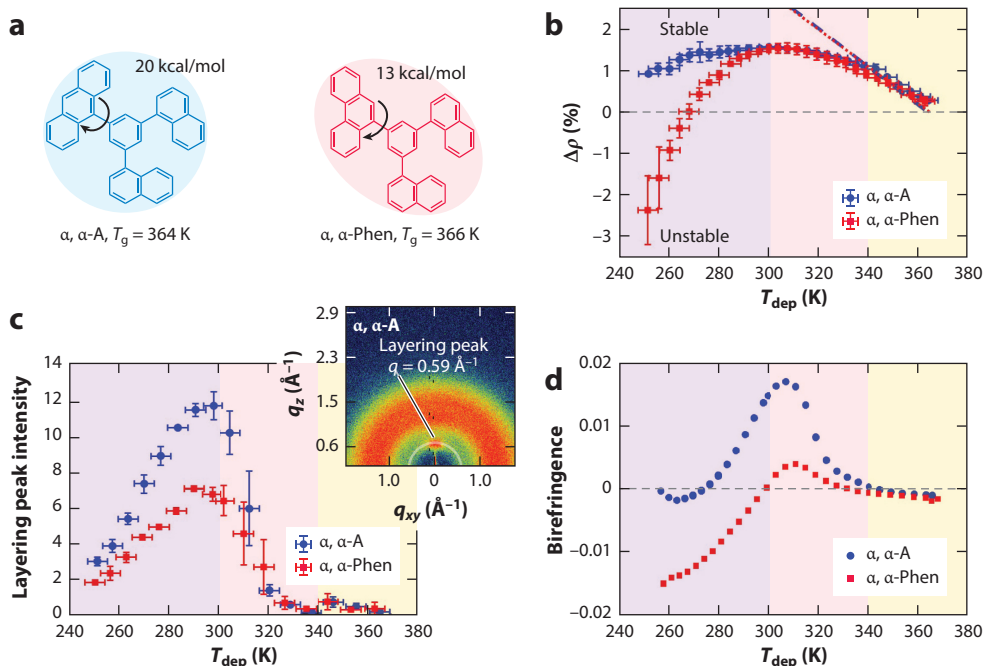


Figure 3

T_{dep} dependence of properties for PVD glasses of two structurally similar molecules, α, α -A and α, α -Phen. (a) Chemical structures of α, α -A and α, α -Phen. The barriers for the dihedral rotations (arrows) are ~ 20 kcal/mol and ~ 13 kcal/mol for the -A and -Phen substituents, respectively (16). (b) Relative density change ($\Delta\rho$) of ~ 240 -nm-thick films of each molecule, deposited at $R_{\text{dep}} = 0.2$ nm/s on temperature-gradient substrates. The dashed blue and dotted red lines represent the corresponding extrapolated SCL values for each molecule. (c) Layering peak intensity versus T_{dep} for ~ 1 - μm -thick films of each glass. (Inset) 2D GIWAXS measurements for an α, α -A film deposited at 298 K. The peak intensity is measured as the intensity of the nonisotropic feature in the q_z direction ($q = 0.59 \text{ \AA}^{-1}$; white arrow), roughly corresponding to the molecular size. (d) Optical birefringence (the difference between the out-of-plane and in-plane indices of refraction) versus T_{dep} for ~ 1 - μm -thick films of each glass. The color-coded regions in panels b–d highlight three regimes of distinct behavior: near-equilibrium (yellow), kinetically trapped (pink), and out-of-equilibrium (purple) structures. Abbreviations: GIWAXS, grazing-incidence wide-angle X-ray scattering; PVD, physical vapor deposition; SCL, supercooled liquid; α, α -A, 9-[3,5-di(naphthalen-1-yl)phenyl]-anthracene; α, α -Phen, 9-[3,5-di(naphthalen-1-yl)phenyl]phenanthrene. Panels b and c adapted with permission from Reference 16; copyright 2022 AIP Publishing. Panel d adapted with permission from Reference 35; copyright 2022 American Chemical Society.

with bulk aging rates. In addition, aging alone does not describe the anisotropic properties of PVD glasses produced in the kinetically trapped and out-of-equilibrium regimes (Figure 3).

The stability and density of PVD glasses often maximize at $T_{\text{dep}} = 0.8\text{--}0.9T_g$ at the typical deposition rate of $R_{\text{dep}} \sim 0.1\text{--}1$ nm/s. Lowering R_{dep} can also increase T_{onset} , decrease T_f (25, 27), and substantially increase the layering peak intensity (14). For low- T_g molecules, R_{dep} can be well controlled in situ over a broader range using a fine leak valve. In these systems, the kinetic stability, often measured as the quasi-isothermal transformation time ($t_{\text{transformation}}$) at a temperature above T_g , eventually saturates at low R_{dep} . For example, $t_{\text{transformation}}$ saturates at $R_{\text{dep}} < 1$ nm/s for ethylcyclohexane deposited at $T_{\text{dep}} > 0.85T_g$ (Figure 4a), indicating that equilibrium conditions are reached in the surface region within the timescale of deposition and thus no further equilibration is possible. This observation is consistent with the fact that isotropic structures are produced at

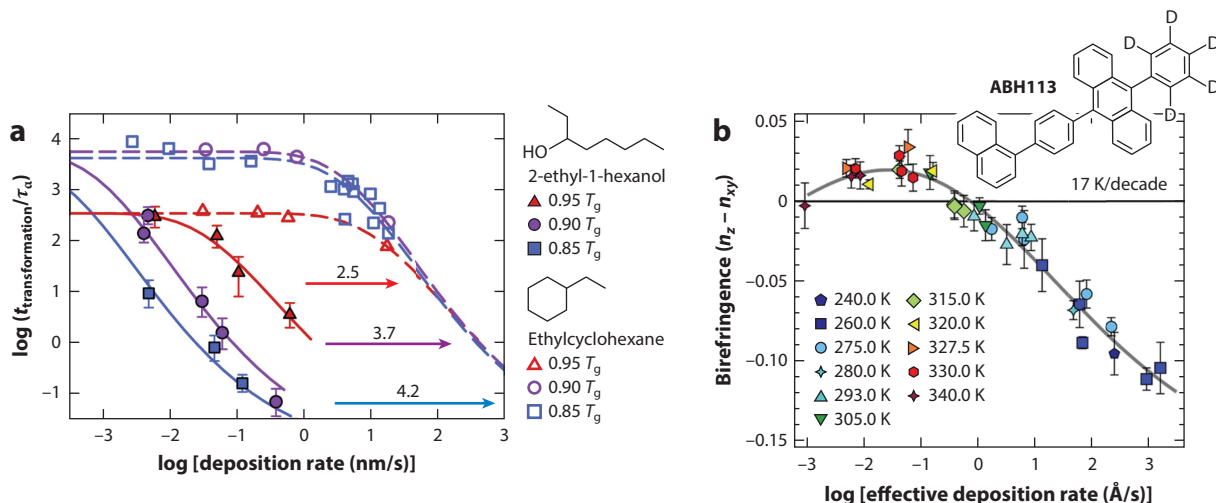


Figure 4

(a) Quasi-isothermal transformation times, measured at approximately T_g , normalized to the α -relaxation time ($t_{\text{transformation}}/\tau_\alpha$) for PVD glasses of 2-ethyl-1-hexanol and ethylcyclohexane (structures shown on the right) as a function of deposition rate. Solid and dashed lines of the same color are stretched exponential fits that have the same plateau values and are horizontally shifted by the number of decades shown above each colored arrow, corresponding to the estimated difference in surface relaxation times for the two molecules at the same relative T_{dep} . (b) RTS measured through birefringence of PVD glasses of ABH113 (chemical structure shown in the inset). Each color represents data for a given T_{dep} , with R_{dep} shifted by 17 K/decade relative to the reference R_{dep} at $T_{\text{dep}} = 293$ K (x axis). Abbreviations: PVD, physical vapor deposition; RTS, deposition rate–substrate temperature superposition. Panel *a* adapted with permission from Reference 85; copyright 2017 AIP Publishing. Panel *b* adapted with permission from Reference 59; copyright 2022 AIP Publishing.

low R_{dep} and high T_{dep} (e.g., **Figure 3c,d**). Therefore, when a plateau can be reached, the inverse of R_{dep} can be used as an effective surface equilibration time at the corresponding T_{dep} (53).

At lower T_{dep} (typically $T_{\text{dep}} < 0.9 T_g$), molecules have less mobility but a larger thermodynamic driving force toward equilibrium, as measured indirectly through the distance from the extrapolated SCL. Therefore, at lower T_{dep} , decreasing R_{dep} (on a logarithmic scale) can have a much larger effect on stability. T_f values equivalent to those of the SCL can be achieved in this region only at extremely low R_{dep} values (66). In metallic glasses, this phenomenon can be extrapolated to even lower T_{dep} values. In zirconium-based metallic glasses deposited at $R_{\text{dep}} = 1.4$ nm/s, the highest T_{onset} , $T_g + 11$ K (32), is obtained at $T_{\text{dep}} = 0.7\text{--}0.8 T_g$. However, Luo et al. (37) demonstrated that for glasses deposited at room temperature (i.e., $T_{\text{dep}} \simeq 0.43 T_g$), decreasing R_{dep} from 0.17 nm/s to 0.017 nm/s can result in an increase up to ~ 60 K in T_{onset} (measured at a heating rate of 20 K/min). Sun et al. (33) observed an increase in T_{onset} of up to ~ 70 K in zirconium-based glasses by decreasing R_{dep} from ~ 4 nm/s to ~ 0.1 nm/s. Enhancement of the crystallization temperature and mechanical performance, as well as structural homogenization, has also been observed following a decrease in R_{dep} (33, 34, 37).

3.2. Rate–Temperature Superposition

A quantitative relationship between R_{dep} and T_{dep} can be built on the basis of the above-described effects (58, 59, 86, 87). Bishop et al. (59) demonstrated that decreasing R_{dep} has the same effect on the molecular orientation as increasing T_{dep} . They built a deposition rate–substrate temperature superposition (RTS) model to predict the orientational anisotropy in liquid crystalline (58, 86)

and non-liquid crystalline PVD glasses (59, 87). **Figure 4b** shows an example of RTS for PVD glasses of ABH113. The birefringence of glasses deposited at various T_{dep} values as a function of R_{dep} is shifted to $T_{\text{dep}} = 293$ K along the x axis with a constant factor of 17 K/decade, meaning that increasing T_{dep} by 17 K produces a glass with the same birefringence as that deposited one-tenth as fast at the original T_{dep} value. The orientation order parameter derived from GIWAXS experiments (S_{GIWAXS}) also obeys RTS with similar shift factors. RTS has been observed for the layering peak position in tris(8-hydroxyquinoline)aluminum (Alq3) molecules, which are spherically shaped (9). Note that both orientation and layering can contribute to positive birefringence (16, 61). Therefore, in systems containing both features, the RTS relationship for layering and anisotropy may differ, making the overall picture slightly less reliable for the deposition region with positive birefringence. However, these are secondary effects, and the RTS relationship is expected to hold overall. The values of both S_{GIWAXS} and birefringence (**Figure 4b**) approach zero at the limiting low R_{dep} value, suggesting that at any value of T_{dep} a sufficiently slow deposition can result in isotropic and near-equilibrium structures.

Few studies have investigated RTS relationships based on density and kinetic stability. Chua et al. (53) used in situ calorimetry to study isothermal transformation dynamics in ethylcyclohexane SGs. They showed that the R_{dep} dependence of $t_{\text{transformation}}$ can be described as a stretched exponential with the same exponent at all T_{dep} values, meeting the necessary condition of RTS. Chua et al. used the plateau in $t_{\text{transformation}}$ at low R_{dep} to estimate the effective surface relaxation times at temperatures as low as $T_{\text{dep}} = 0.6T_g$, well below the Kauzmann temperature, $T_K \sim 0.76T_g$. A similar strategy has been used for other molecular SGs (78, 85). In metallic glasses, Luo et al. (37) observed the plateau of T_{onset} at $R_{\text{dep}} < 0.017$ nm/s at $T_{\text{dep}} = 0.43T_g$, indicating an enhanced surface equilibration rate at these extremely low temperatures. These studies are important for two reasons. First, direct measurements of surface mobility at low temperatures are extremely difficult, even for LQG surfaces, and can depend strongly on the nature of the dynamical gradients (70, 88, 89). Second, recent simulations indicate that surface mobility profiles are anisotropic and may differ on the SG and LQG surfaces (16). As such, these indirect measures of effective surface equilibration times are critical not only for predicting SG formation but also for understanding its underlying glass physics.

When testing RTS based on T_f and density, one should note that the values of the relevant parameters at the limiting low R_{dep} value may vary with temperature, making direct comparisons of data at various T_{dep} values more difficult, particularly if an unknown phase change exists (69, 90). Therefore, this approach may not be generalizable. In contrast, optical birefringence, orientation order parameter (S_z), and layering become zero (isotropic) for a fully equilibrated bulk glass, setting a common limiting value at slow R_{dep} . However, in the latter case there is still an underlying assumption that any low-temperature equilibrium phase is also isotropic, which is not generally known. A puzzling but interesting observation by Chua et al. (53) is that the limiting values of $t_{\text{transformation}}$ decrease when T_{dep} is reduced below $0.85T_g$. This observation would not be expected if the state reached in this limit were the same as the corresponding SCL. These authors proposed that slow deposition equilibrates the glass with respect to its surface structure, which can be higher in free energy than the bulk SCL.

3.3. The Effect of Chemical Structure

RTS relationships offer powerful evidence that enhanced surface mobility controls stability during PVD. By investigating the role of variations in chemical motifs, such as changes in molecular shape (**Figure 3**), intramolecular flexibility, and intermolecular interactions, we can gain additional insight into the surface equilibration process and its role in SG formation.

3.3.1. Intermolecular interactions. An increase in intermolecular interaction generally decreases surface mobility and the degree of stability achieved upon PVD. At the same relative T_{dep} and R_{dep} , PVD glasses of ethylcyclohexane have higher kinetic stability than 2-ethyl-1-hexanol and are much less affected by R_{dep} in the range of values studied (**Figure 4a**). PVD glasses of 2-ethyl-1-hexanol have little to no kinetic stability ($t_{\text{transformation}} < \tau_{\alpha}$) at the typical deposition conditions of $T_{\text{dep}} \sim 0.85T_{\text{g}}$ and $R_{\text{dep}} = 0.1\text{--}1\text{ nm/s}$, and they show stability only when R_{dep} is further reduced. This contrasting behavior can be attributed to the intermolecular hydrogen-bond formation in 2-ethyl-1-hexanol (85), which lowers its surface mobility and thus requires longer surface equilibration times to achieve a similar degree of stability (85). Laventure et al. (81) studied the kinetic stability of several hydrogen-bonding molecules and demonstrated that a molecule with more extensive hydrogen bonding has a reduced ability to form SGs. Chen et al. (75) measured the surface diffusion of these molecular glasses and demonstrated a direct correlation between reduced surface diffusion and SG formation (for more details and discussion, see Section 4) (**Figure 7a**).

Moore et al. (51) used coarse-grained molecular dynamics (MD) simulations to explore the stability of molecules containing fluoroalkyl chains of varying lengths. They found that increasing the fluoroalkyl tail length promotes segregation of fluorine-containing domains to the glass surface and causes microstructure formation throughout the PVD film. Together, these effects result in reduced surface diffusion and slower surface relaxation dynamics in systems with increased fluoroalkyl tail length, thus reducing the molecules' ability to form SGs upon PVD.

3.3.2. Molecular shape and orientation. Molecular orientation in glasses of nonspherical molecules can be probed through measurements of optical birefringence using SE (5, 8, 13) and orientation order parameters obtained either in SE and optical absorption measurements (S_z) (8, 10, 57) or in GIWAXS experiments (S_{GIWAXS}) (15). **Figure 5a** shows the T_{dep} dependence of S_z for PVD glasses of different molecular shapes measured using SE. S_z describes the average orientation of the molecular axis of symmetry relative to the substrate normal. The axis of symmetry is along the molecule's length in rodlike molecules and normal to the molecule's plane in disklike molecules (**Figure 5a, inset**). Thus, a perfect horizontal orientation corresponds to $S_z = -0.5$ for rodlike molecules and $S_z = 1$ for disklike molecules, and a perfect vertical orientation corresponds to $S_z = 1$ for rodlike molecules and $S_z = -0.5$ for disklike molecules. $S_z = 0$ indicates isotropic packing (8). **Figure 5a** shows that in both rodlike (10) and disklike (8) molecules, at a fixed R_{dep} value, a decrease in T_{dep} leads to variation in the preferred orientation of molecules, ranging from isotropic at $T_{\text{dep}} \sim T_{\text{g}}$ to slightly out of plane at $0.9T_{\text{g}} < T_{\text{dep}} < T_{\text{g}}$ to predominantly in plane for $T_{\text{dep}} < 0.9T_{\text{g}}$. Lyubimov et al. (11) observed the characteristic T_{dep} dependence of S_z in coarse-grained MD simulations of N, N' -bis(3-methylphenyl)- N, N' -diphenylbenzidine (TPD) SGs, which demonstrates similar effects when R_{dep} is increased at constant T_{dep} . These findings are consistent with the measured optical birefringence for a wide range of molecules, such as α, α -Phen (**Figure 3d**) and ABH113 (**Figure 4b**), and are in agreement with the RTS relationship.

To understand the origin of orientational order in PVD glasses, it is helpful to investigate the equilibrium configurations of the topmost layers of a SCL. Walters et al. (8) used MD simulations to evaluate S_z at the SCL surface of simulated rodlike and disklike molecules and compared their data with the corresponding experimental values measured in PVD films (**Figure 5b**). At the free surface, the long axis of molecules tends to lie in the plane of the film as a result of the constraints imposed by a flat interface, which restricts the ability of molecules to freely rotate. At a depth of $\sim 1\text{ nm}$ away from the free surface (roughly the size of each molecule), S_z changes sign, indicating a tendency for the molecules' long axis to orient perpendicular to the free surface. The strong correlation between the T_{dep} dependence of S_z and the orientation of the molecules at the SCL

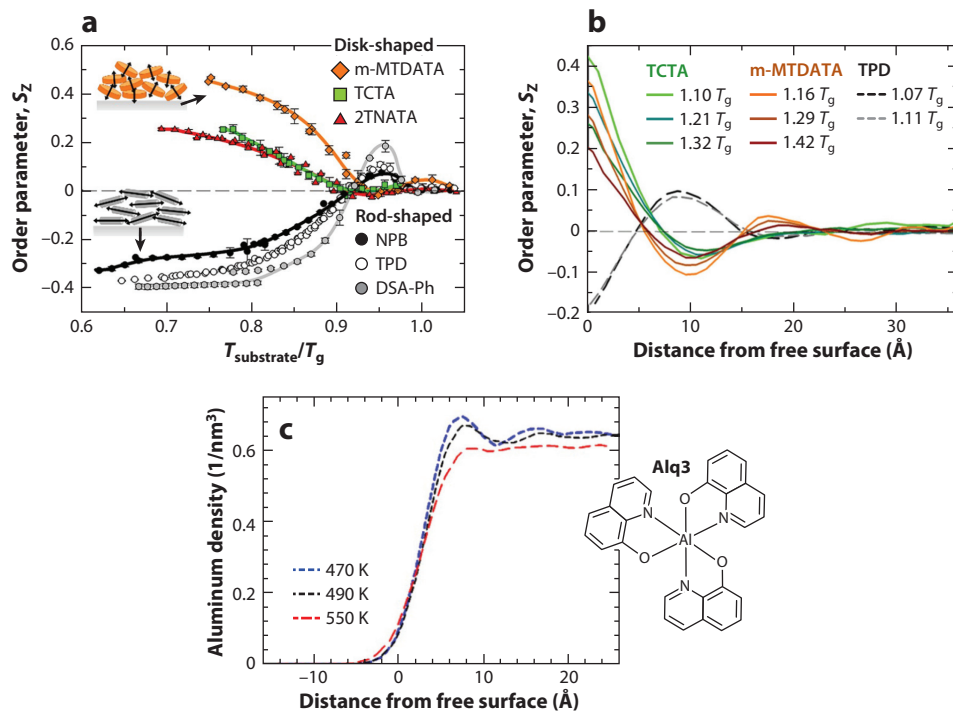


Figure 5

(a) S_z versus relative T_{dep} for disklike (m-MTDATA, TCTA, and 2TNATA) and rodlike (TPD, NPB, and DSA-Ph) molecules. The axis of symmetry for each shape is shown in the inset. (b) Simulated S_z versus distance from the free surface, at various temperatures above T_g . The positive and negative values of S_z for the disklike and rodlike molecules, respectively, indicate that the long axes of these molecules preferentially orient along the plane of the film near the free surface. Further into the liquid, around 10 Å, the sign of S_z changes, indicating perpendicular orientation. Further away, the SCL becomes isotropic ($S_z = 0$). (c) Aluminum density versus distance from the free surface in a simulated Alq3 SCL ($T_g = 450$ K; structure shown to the right of the graph) at various temperatures. Increasingly strong oscillations of aluminum density are evident upon cooling, indicating layered structures. Abbreviations: Alq3, tris(8-hydroxyquinoline) aluminum; DSA-Ph, 1-4-di-[4-(N,N' -diphenyl)amino]styryl-benzene; m-MTDATA, 4, 4', 4''-tris[(3-methylphenyl)phenylamino]triphenylamine; NPB, N,N' -di(1-naphthyl)- N,N' -diphenyl-(1,1'-biphenyl)-4,4'-diamine; SCL, supercooled liquid; S_z , orientation order parameter; TCTA, tris(4-carbazoyl-9-ylphenyl)amine; TPD, N,N' -bis(3-methylphenyl)- N,N' -diphenylbenzidine; 2TNATA, 4, 4', 4''-tris[2-naphthyl(phenyl)amino]triphenylamine. Panels *a* and *b* adapted with permission from Reference 8; copyright 2017 American Chemical Society. Panel *c* adapted with permission from Reference 9; copyright 2018 American Chemical Society.

surface suggests that molecular orientation at the free surface is preserved into the bulk glass. When PVD is performed at fast rates or at low T_{dep} , only the top monolayer of the film can equilibrate at the timescale of deposition. Therefore, the PVD glass is arrested in a configuration that is representative of the structure of this layer, and the glass is either unstable or only moderately stable, because the equilibrium state at the boundary differs from that of isotropic bulk glass (53). The rest of the glass, even the layer directly below the free surface, is effectively out of equilibrium. As R_{dep} is reduced or T_{dep} is increased, molecules in the second layer are able to equilibrate, allowing partial reorientation. Thus, the glass adopts a structure with an out-of-plane orientation and moderately more stable states. Lastly, when T_{dep} is close to T_g , or when R_{dep} is sufficiently low (Figure 4b), isotropic structures are obtained. This requires reorientation and equilibration of

molecules at even greater distances from the free surface, thus indicating that the thickness of the mobile surface layer, with an effective local T_g lower than T_{dep} , is at least a few monolayers thick.

3.3.3. Molecular layering. In contrast to the orientational anisotropy, molecular layering has not been linked to a specific chemical motif in PVD glasses (10, 13–15, 80). Layering typically refers to a distinct anisotropic peak in GIWAXS experiments of SGs (e.g., **Figure 3c**, *inset*). This feature is observed even in PVD glasses of small size and in spherical molecules that do not show orientational order (9, 16, 40, 61). While layering is correlated with positive optical birefringence in some spherically shaped molecules, such as α , α -A (16) (**Figure 3c,d**), this relationship is not general (9, 10, 13, 15) and layering appears to be independent of the orientational order. However, both layering and orientation contribute to the optical birefringence values (e.g., in α , α -Phen; **Figure 3c,d**), which can also be influenced by factors such as a strong dipole–dipole coupling between the oriented molecules (91).

Layering has been attributed to two potential factors. One possible origin is inheriting the layered molecular packing from the equilibrium liquid surface (9), analogous to the formation of the orientational order. **Figure 5c** shows an example of this form of molecular layering in a simulated SCL of Alq3 molecules, where, upon decreasing the temperature toward T_g , surface oscillations in aluminum density are developed and become increasingly pronounced. This form of surface-induced layering has also been observed in SCL states of metallic (92), ionic (93), and molecular (94) glasses. However, surface-induced layering does not adequately describe all aspects of experimental observations. For example, if molecular layering were due solely to the equilibrium surface structure, one would expect to see a larger degree of surface-induced layering as T_{dep} decreases, similar to in-plane orientational order. However, the layering peak intensity is typically nonmonotonic, meaning that the largest degree of layering occurs at intermediate T_{dep} values (**Figure 3c**). As T_{dep} is decreased, the extent of layering decreases rapidly toward zero, while stronger rapidly in-plane orientation is adopted.

We recently proposed an alternative origin for layering as the accelerated aging of the interfacial region, under the constraint of the immobile glass layer beneath (16). Aging under constraint can result in anisotropic properties, where molecules can pack more readily in the vertical direction than in the lateral direction, under tensile stress. This hypothesis is strengthened by the observation that for the structurally similar molecules α , α -A and α , α -Phen, the growth of the layering peak coincides with T_{dep} values at which the glass can no longer reach equilibrium at the timescale of deposition. The origin of layering and its specific structure merit more detailed studies, which could identify pathways for equilibration that are not strongly tied to the equilibrium mobility of the free surface layer.

3.3.4. Intramolecular flexibility. Few studies have systematically investigated the role of molecular flexibility in stability. For example, α , α -A and α , α -Phen have similar molecular weights and intermolecular interactions but have different barriers to dihedral rotation, which are calculated to be ~ 20 kcal/mol for the -anthracene (-A) substituent of α , α -A and ~ 13 kcal/mol for the -phenanthrene (-Phen) substituent of α , α -Phen (16) (**Figure 3a**). For $T_{dep} > 0.82T_g$, these molecules show similar degrees of thermodynamic stability. However, at lower T_{dep} values, the stability of α , α -Phen falls dramatically while α , α -A remains stable even at the lowest T_{dep} of 251 K ($0.69T_g$), with $\Delta\rho \sim 1\%$. This finding is surprising because α , α -Phen is more kinetically stable and has greater surface mobility close to T_g , as indirectly measured through dewetting experiments (16).

To understand this phenomenon, we performed coarse-grained MD simulations on model α , α -A molecules with various energy barriers for dihedral rotations defined as $E_d = K[1 + \cos(n\phi)]$ (**Figure 6a**). Setting $K = 50$ represents a more rigid version of α , α -A, and setting $K = 0$

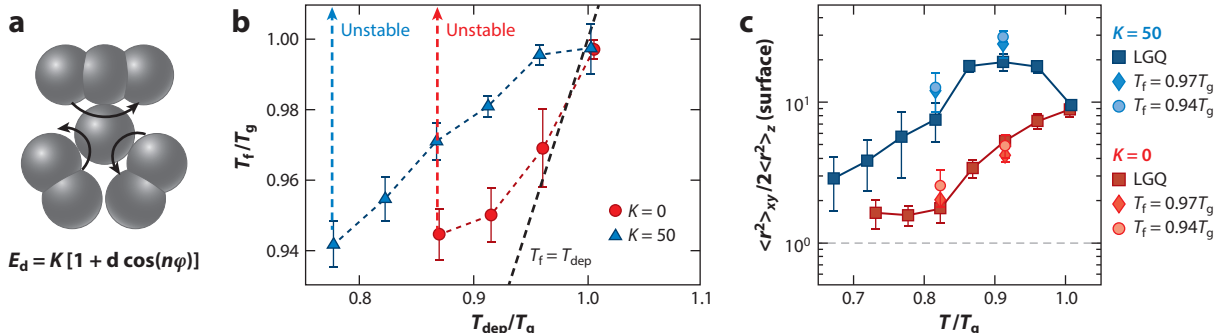


Figure 6

Mobility anisotropy and stability of simulated glasses with various rigidities. (a) Coarse-grained model of α, α -A. The arrows represent dihedral rotations. $K = 50$ represents a more rigid version of α, α -A, and $K = 0$ represents a more flexible version of α, α -Phen. (b) Relative T_f/T_g versus relative T_{dep}/T_g for simulated PVD glasses with $K = 0$ (red) and $K = 50$ (blue). The dashed black line indicates $T_f = T_{dep}$ (extrapolated SCL). The dashed arrows represent T_{dep} , below which unstable glasses are formed with $T_f > T_{dep}$. (c) Surface mobility anisotropy, measured as the ratio of the in-plane ($\langle r^2 \rangle_{xy}$) and out-of-plane ($\langle r^2 \rangle_z$) mean squared displacement, versus T/T_g for glass films with $K = 0$ (red) and $K = 50$ (blue). Data for LGQ films (dark squares connected by solid lines) as well as two different PVD films, with $T_f = 0.97T_g$ (diamonds) and $T_f = 0.94T_g$ (light circles), are presented. Abbreviations: LGQ, liquid-quenched glass; PVD, physical vapor deposition; SCL, supercooled liquid; α, α -A, 9-[3,5-di(naphthalen-1-yl)phenyl]anthracene; α, α -Phen, 9-[3,5-di(naphthalen-1-yl)phenyl]phenanthrene. Figure adapted with permission from Reference 16; copyright 2022 AIP Publishing.

represents a more flexible version of α, α -Phen. The results indicate that, similar to the experiments, PVD glasses of $K = 0$ molecules are more stable at high T_{dep} but also more rapidly lose their ability to form SGs as T_{dep} is reduced (Figure 6b). Investigation of the SCL surface of these molecules shows that, unlike the bulk liquids, the surface molecules have significant mobility anisotropy, with faster in-plane than out-of-plane motion (95). Interestingly, the flexible molecules ($K = 0$) show a rapid decrease in their surface mobility anisotropy, which becomes nearly isotropic at $T = 0.82T_g$. This is the same temperature where their corresponding PVD glasses become unstable (Figure 6c). In contrast, the rigid molecules maintain higher mobility anisotropy values over a broader range of temperatures, corresponding to the broader T_{dep} range where they can form SGs. Moreover, these glasses have more pronounced mobility anisotropy on their PVD glass surfaces in comparison to their SCL surface. The reduced mobility anisotropy in the $K = 0$ molecules is accompanied by overall slower surface mobility in the lateral direction (16). These results suggest that, while at higher T_{dep} the flexible molecules can access more configurations and have enhanced surface mobility to produce SGs, at lower T_{dep} their dynamics can more efficiently couple with the glass layers underneath, resulting in reduced mobility, weaker mobility gradients, and weaker mobility anisotropy, which collectively result in the production of unstable glasses. These results, as well as previous experimental data (96, 97), indicate that the thickness of the mobile layer and its mobility gradients are not static functions and are strongly influenced by the kinetic facilitation of both the free surface and the rigid glass underneath. The evidence of kinetic facilitation has also been observed in T_g measurements of polymer thin films (89, 98–100) and in transformation kinetics of SGs capped with a PVD layer of a molecule with higher T_g (101–104).

4. DIRECT MEASUREMENTS OF GLASS SURFACE MOBILITY

Given the broad range of gradients in mobility and their strong dependence on temperature, direct characterization of the surface relaxation dynamics, mobility gradients, and mobility anisotropy

is extremely challenging. However, combinations of elegant experimental methods and MD simulations have provided significant insight into these processes.

4.1. Surface Diffusion Measurements

In experiments, surface diffusion can be obtained by monitoring the change in surface morphology as a function of time. Examples include measurements of the decay of surface grating patterns and the formation of menisci around probe particles. Grating decay experiments are suitable for bulk LQG and aged films, which are then compared with the degree of stability of PVD glasses measured separately. However, to directly measure diffusion on PVD glass surfaces, one needs a less disruptive strategy than embossing gratings. In these systems, placing probe particles can produce time-varying menisci that can be used to measure surface diffusion. Here, we review the outcomes of these measurements and their ability to predict SG formation.

4.1.1. Surface diffusion of liquid-quenched glasses. Lateral surface diffusion of LQGs has been extensively studied in experiments and simulations of molecular, polymeric, and metallic glasses (65, 71, 72, 105–107). In grating decay experiments on the surface of an expansive set of molecules, Yu and colleagues (71, 75, 108–111) distinguished surface diffusion from viscous relaxation through the wavelength dependence of the grating decay rate. For a grating with a wavelength of λ , viscous flow induces a decay rate that scales with λ^{-1} , while the decay rate of surface diffusion, defined as the slip-free motion of the top monolayer, scales with λ^{-4} . This strong wavelength dependence, corresponding to surface diffusion, is observed only at low temperatures, where the rest of the glass is out of equilibrium and the viscous flow rate is too slow to be dominant. We also note that a no-slip condition of the lateral motion of molecules is necessary in order for this scaling to be preserved. This means that the participating molecules need to have the same velocity and, thus, are likely within only one or two layers of the surface. Therefore, they cannot represent a thick layer with mobility gradients below the free surface (106).

Figure 7a compares the measured surface diffusion coefficient (D_s) with the bulk diffusion coefficient (D_v) (112–114) for various molecules. While the T_g/T dependence of D_v is generally independent of molecular weight and shows strong non-Arrhenius behavior, D_s shows Arrhenius behavior and is significantly enhanced, exceeding D_v by up to eight orders of magnitude at T_g . Given the lower activation energy of D_s in comparison to D_v , these differences increase at lower temperatures. Furthermore, on the surface of highly aged glasses, where bulk diffusion and relaxation dynamics are even slower, surface diffusion remains fast and independent of aging time (74). In addition, unlike D_v , D_s strongly depends on the molecular weight, decreasing significantly in larger molecules and polymers, as the molecules are partially trapped in the slower layers below the free surface (**Figure 7a**). Strong intermolecular interactions such as hydrogen bonding (108) and network formation (51) can also decrease D_s , eliminating surface diffusion in systems with extensive hydrogen bonding (the upper-bound values are shown in **Figure 7a**) (108). Liu et al. (115) found that the addition of even a small amount (5 % mass percentage) of hydrogen-bond-forming molecules is enough to significantly suppress D_s .

While some computational studies have suggested that surface diffusion is the main mode of PVD equilibration (52, 116) and experiments have demonstrated a correlation between D_s and stability in some hydrogen-bonding systems (75, 108), enhanced surface diffusion is not adequate to explain the large degree of stability and the ubiquitous nature of SG formation during PVD. For example, Laventure et al. (81) found that for NHMe [2-methylamino-4,6-bis(3,5-dimethyl-phenylamino)-1,3,5-triazine], a strongly hydrogen-bonding molecule, surface diffusion is not observed and its PVD glasses have lower kinetic stability than other systems. However, this

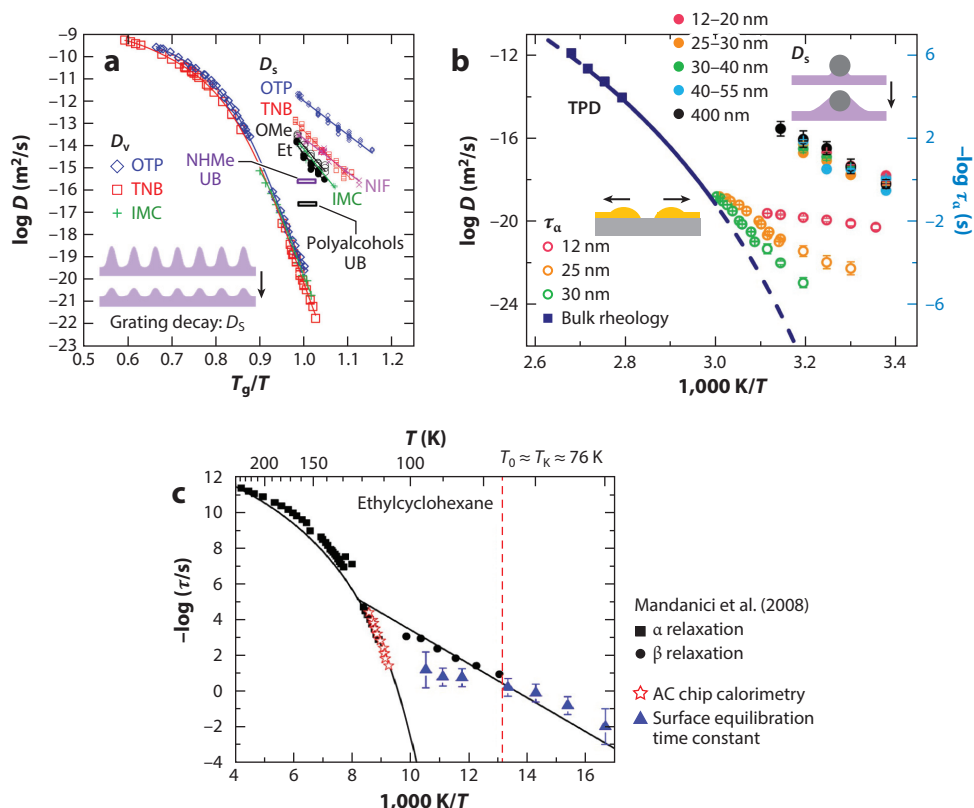


Figure 7

(a) D_v and D_s versus T_g/T for LQGs of various molecules. D_s is measured in grating decay experiments (shown schematically in the inset). For NHMe and polyalcohols, surface diffusion is not observed, and only UB values are reported. (b) D_s for TPD glass films of various thicknesses (*left axis, filled circles*) measured using meniscus formation around a probe particle (shown schematically in purple), plotted along with average bulk relaxation times τ_α (*right axis*) measured using bulk rheology (*dark blue squares*), dielectric spectroscopy (*solid dark blue line*), CR- T_g , and dewetting (schematically shown in yellow) for films of various thicknesses (*open circles*). While D_s is independent of film thickness, τ_α strongly decreases with decreasing film thickness and becomes significantly faster than bulk at low temperatures. (c) Surface equilibration time of ethylcyclohexane derived from the R_{dep} dependence of SG stability (*triangles*), along with dynamic T_g (*stars*) from AC calorimetry and the α -relaxation (*squares*) and β -relaxation times (*circles*) from dielectric measurements. T_0 and T_K (from calorimetry) are shown as a reference (*dashed red line*). Abbreviations: CR- T_g , cooling-rate-dependent T_g ; D_s , surface diffusion coefficient; D_v , bulk diffusion coefficient; Et, 2-ethyl-4,6-bis(3,5-dimethyl-phenylamino)-1,3,5-triazine; IMC, indomethacin; LQG, liquid-quenched glass; NIF, nifedipine; NHMe, 2-methylamino-4,6-bis(3,5-dimethyl-phenylamino)-1,3,5-triazine; OMe, 2-methoxy-4,6-bis(3,5-dimethyl-phenylamino)-1,3,5-triazine; OTP, *ortho*-terphenyl; SG, stable glass; TNB, 1,3-bis-(1-naphthyl)-5-(2-naphthyl)benzene; TPD, N, N'-bis(3-methylphenyl)-N, N'-diphenylbenzidine; UB, upper bound. Panel *a* adapted with permission from Reference 75; copyright 2017 American Chemical Society. Panel *b* adapted with permission from Reference 117; copyright 2017 National Academy of Sciences. Panel *c* adapted with permission from Reference 53; copyright 2015 AIP Publishing.

molecule can still form glasses with high density and layering structures at moderate T_{dep} values, indicating its ability to equilibrate during PVD.

4.1.2. Surface diffusion of stable glasses. To better understand the role of surface diffusion in stability, one needs to directly measure D_s on the surface of SGs. Our group has developed a

method based on measurements of meniscus formation around elongated probes (*Tobacco mosaic virus* and gold nanorods) (76, 106) that can be performed directly on SG surfaces. The rate of meniscus formation follows a similar scaling law as the grating decay rate and thus can distinguish lateral surface diffusion from other modes of surface relaxation. For example, viscous relaxation causes the probe to sink into the film. TPD molecules deposited over a broad range of T_{dep} produce SGs with a wide range of thermodynamic stability, with values of T_f ranging between T_g and $T_g - 35$ K. The estimated bulk relaxation times of these films span 10–20 decades in extrapolated values. However, in these films, D_s measured at various temperatures below T_g is independent of T_f and identical to that measured on the LQG surface. While the bulk glass can reach low-energy states upon PVD, surface diffusion remains unchanged and orders of magnitude faster, resulting in a more dramatic dynamical difference between D_s and D_v in SGs than in LQGs. Interestingly, when these measurements are extended to thin LQG films, where the average relaxation dynamics are enhanced by 4–6 decades compared with bulk, D_s is still invariant and independent of the film thickness (**Figure 7b**), even when a film is visibly dewetting as a result of its enhanced mobility while D_s is being measured (117).

We have also studied SG surface diffusion in two structurally similar organic molecules, 1,3-bis-(1-naphthyl)-5-(2-naphthyl)benzene (TNB) and α , α -A, both of which form SGs at a broad range of T_{dep} values (76). SGs of these two molecules with similar degrees of stability show markedly different surface diffusion behaviors. In TNB D_s is enhanced in both LQG and PVD films, while in α , α -A there is no evidence of enhanced surface diffusion in either state. These observations indicate that enhanced surface diffusion is neither necessary nor sufficient to produce SGs, as the motion of the topmost surface molecules appears to be independent of the degree of stability and not a necessary condition for SG formation.

4.2. Relaxation Dynamics Near the Free Surface

Measurements of relaxation dynamics below the immediate free surface of molecular glasses can be a challenging task. Surface relaxation dynamics can be anisotropic and can depend on the degree of glass stability (**Figure 6c**). Furthermore, considering that surface diffusion is enhanced by up to 8 decades while the center of the SG film is in an equilibrated state, analogous to 5–10 decades of physical aging, the relaxation dynamics can span a range of 10–15 decades within a few nanometers of the free surface. Therefore, measurements using various methods can sample these gradients differently, making data interpretation more challenging. However, methods have been developed in the past 30 years particularly to measure relaxation dynamics of polymer surfaces, for example, by monitoring the filling of nanodeformations (70, 118), embedding of nanoparticles (119–121), tracking the evolution of surface morphology (122, 123), and recovery after photobleaching (124). These measurements indicate that below a certain temperature, typically a few degrees above T_g , the glass surface exhibits faster relaxation dynamics with lower activation energy (i.e., lower fragility) than the inner bulk layers (70, 124). Thus, the difference between the surface and bulk relaxation dynamics increases significantly as the temperature decreases below bulk T_g . These effects can propagate into the free surface over a distance of a few nanometers close to $T_g(\text{bulk})$ (119, 124). Interestingly, when measurements are performed well above T_g , the relaxation dynamics of the free surface and bulk do not dramatically differ, and differences arise only close to and below bulk T_g . The reason for this phenomenon is not well understood, as most theories predict enhanced dynamics at all temperatures (65, 125, 126), with relaxation times that are a function of the bulk relaxation time. As such, they predict a more moderate degree of enhancement than is experimentally measured. Evidence from thin-film experiments suggests that cooperative effects between the bulk and surface dynamics may be at play (96, 97).

In a study of metallic glasses, Chatterjee et al. (127) used electron correlation microscopy to measure interfacial relaxation dynamics of nanowires and demonstrated an ~ 20 K reduction in the free surface T_g , which was eliminated when the surface was capped. Ashtekar et al. (128–130) measured cooperative rearrangements involving a few atoms on metallic glass surfaces below T_g and demonstrated that they have activation energies as low as $\sim 3k_B T_g$, indicating significantly lower fragility at the free surface. These observations are consistent with the formation of metallic SGs at low T_{dep} when R_{dep} is reduced (37). Transmission electron microscopy studies in amorphous silica and silicon nanotubes (131) as well as metallic glasses (132) also demonstrated the existence of an ~ 1 -nm-thick near-surface layer with orders-of-magnitude-enhanced mobility, leading to fluidlike behavior (131, 133). Simulations of metallic glasses showed that the surface atoms exhibit enhanced vibrations (95) with a low-frequency shift of the vibrational density of states (134), suggesting phonon softening at the glass surface.

4.2.1. Thin-film T_g and viscosity measurements. It is difficult to extend many of these techniques to molecular glass surfaces, as surface diffusion tends to dominate properties. Instead, measurements of cooling-rate-dependent T_g (CR- T_g) and dewetting experiments in thin films can be used as a convenient proxy (89). CR- T_g provides an indirect measure of the temperature dependence of τ_α . Viscosity, measured in dewetting experiments, is also proportional to τ_α in molecular glasses. Both quantities are significantly influenced by surface mobility as the film thickness decreases (96, 97). An exhaustive review of T_g measurements in glass thin films (98) is outside the scope of this review, but it is informative to consider a few key observations.

In polymer thin films supported on substrates with weak interactions, a substantial depression of T_g is generally observed as the film thickness decreases (88, 89, 135–137). The T_g suppression can be eliminated by capping these films with a thin metal layer, demonstrating that this effect is caused mainly by the free surface (138). CR- T_g experiments in these films show that as the film thickness decreases, the average activation energy for relaxation (i.e., fragility) decreases dramatically (88, 89, 99), approaching the free surface values measured directly (70, 88). Similar to direct measurements of relaxation times, these effects are observed only at low temperatures with an onset that is a few degrees Kelvin above $T_g(\text{bulk})$, above which bulk and thin-film T_g values are similar.

Our group performed CR- T_g measurements in TPD thin films on various substrates (96, 97, 117) (**Figure 7b**) and observed behavior remarkably similar to that of polymer thin films. Below an onset temperature a few degrees above $T_g(\text{bulk})$, decreasing the TPD film thickness results in lower apparent fragility, while at higher temperatures and in films thicker than ~ 50 nm, the dynamics are bulklike. Notably, in films supported on weakly interacting substrates, when the thickness is decreased below ~ 20 nm, the mobility is so fast that these films behave like an ideal liquid and dewet at the timescale of experiments (76, 97). Dewetting measurements in these films were performed to directly evaluate the effective film viscosity and relaxation times. The temperature dependence of dewetting rates follows a similar trend as CR- T_g (**Figure 7b**), allowing measurements in a broader range of film thicknesses and relaxation times. Enhanced surface diffusion is also observed in these films and follows the bulk temperature dependence. Surprisingly, the activation energy and fragility of thin films can be lower than that of surface diffusion (**Figure 7b**), resulting in a complete decoupling of these two effects (117). Bell et al. (139) observed that films of glassy 3-methylpentane have lower viscosity at the free surface than in the bulk. In these films, the surface viscosity is lower than bulk viscosity but continuously increases toward the corresponding bulk value over a distance of ~ 3 nm.

4.2.2. Relaxation dynamics on stable glass surfaces. To the best of our knowledge, no direct measurements of relaxation dynamics have been performed on SG surfaces. By modeling the

R_{dep} dependence of $t_{\text{transformation}}$ of PVD glasses of ethylcyclohexane, Chua et al. (53) indirectly estimated surface equilibration times (τ_{surface}) during SG formation. The estimated τ_{surface} values appear to have a lower activation energy than bulk, with the degree of enhancement decreasing for T_{dep} close to T_g (**Figure 7c**). These measurements assume that only the top monolayer of molecules is involved in the equilibration process. However, if the thickness of the contributing mobile layer increases with increasing temperature (124), then the actual values of mobility at the immediate free surface should be lower than this estimate when T_{dep} is closer to T_g , as more layers are contributing to equilibration. Therefore, accounting for variable thickness of the mobile layer further reduces the estimated surface activation energy, so the reported value here can serve as an upper bound. This behavior is more similar to the measured surface relaxation times than surface diffusion coefficients, which should be decades faster for this molecule. It is also notable that the τ_{surface} values smoothly change as T_{dep} falls below T_0 . T_0 , which is approximately similar to T_K , is the Vogel–Fulcher–Tammann temperature, at which the bulk relaxation dynamics are expected to diverge (140) or be extremely slow. However, the relaxation dynamics of the surface remains enhanced, strongly indicating that τ_{surface} is not a direct function of τ_{α} , as some theories have predicted (65, 125, 126, 141). These indirect results imply that surface relaxation dynamics play a significant role in surface-mediated SG formation.

4.2.3. Thickness of the mobile layer. Moore et al. (51) used the reorientation of fluoroalkyl chains in simulated PVD glasses to estimate the thickness of the mobile layer. As discussed in Section 3.3.1, for molecules with long fluoroalkyl chains, both surface diffusion and surface relaxation dynamics slow down as a result of microstructure formation and clustering of the tail groups as well as the segregation of fluoroalkyl chains to the free surface. However, despite their slower relative relaxation dynamics compared with molecules with shorter chains, these molecules still show significant rearrangement below the immediate free surface during PVD. **Figure 8a** shows the simulated orientation order parameter [$P_1(z)$] of molecules containing eight fluorine atoms, as a function of distance from the free surface. At the immediate free surface, the fluoroalkyl tails segregate, resulting in a positive value of $P_1(z)$ (**Figure 8a**) that indicates a predominantly vertical orientation of the surface molecules. As the deposition continues and the molecules experience a more isotropic interaction environment, they rearrange and reorient toward the equilibrium $P_1(z) = 0$ value (isotropic packing), which is eventually achieved at a distance of $\sim 10\sigma$ from the free surface, corresponding to 4–5 molecular sizes. Remarkably, despite deposition well below T_g and the relative lack of stability of these films, rearrangement is still observed in the simulation time frame, at such long distances from the free surface.

While no direct experimental measurements of molecular reorientation have been reported, the change in anisotropy as a function of T_{dep} and R_{dep} is consistent with a changing thickness of the mobile layer (see Section 3.2) (10, 11). Variations in the thickness of the mobile layer have been measured indirectly through the intermixing of deuterated and protonated TNB molecules (3), indicating that the thickness of the mobile layer decreases from 3–4 nm close to T_g to one monolayer at lower T_{dep} values. Cao et al. (143) used a tilted monolayer of colloidal suspension to mimic vapor deposition and found that particles at a depth of 14–100 particles from the surface can more frequently relax via cooperative rearrangements involving larger and more anisotropic regions compared with the bulk. Thoms et al. (142) recently performed in situ measurements of dielectric capacitance (ΔC) and dissipation ($\Delta \tan \delta$) during PVD of 2-methyltetrahydrofuran (MTHF) molecules ($T_g = 91$ K) at $R_{\text{dep}} = 0.10$ nm/s. At $T_{\text{dep}} = 75$ K ($0.82T_g$), $\Delta \tan \delta$ rapidly increases during the first $t = 25$ s with the deposition of a 2.5-nm-thick film, after which it gradually transitions to a constant slope for the remaining duration of deposition (**Figure 8b**). This observation indicates that the first 2.5-nm layer of MTHF is in a state with higher residual mobility,

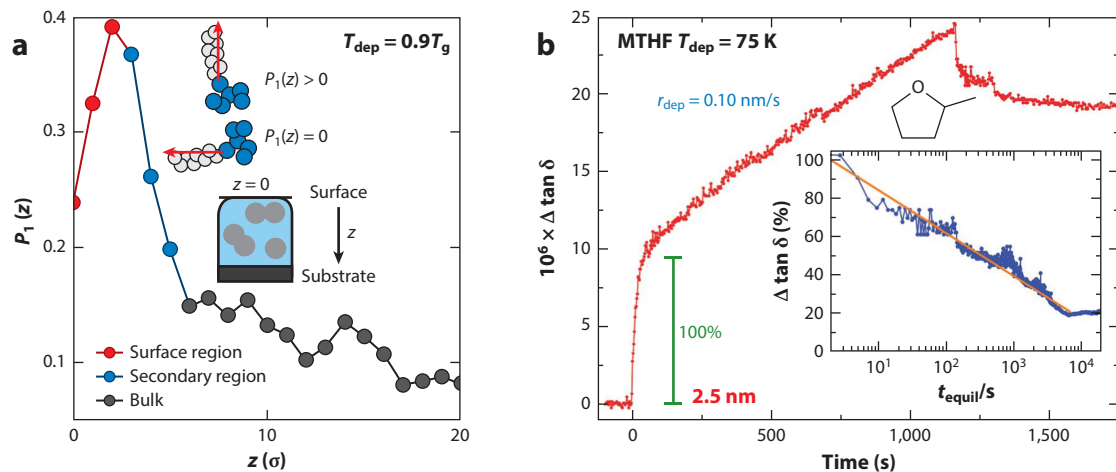


Figure 8

(a) $P_1(z)$ for a fluoroalkyl-containing molecule with eight fluorine atoms versus distance from the glass surface [$z(\sigma)$, where σ is the size of the head-group atoms]. The inset shows molecular orientations corresponding to $P_1(z) > 0$ (oriented toward the free surface) and $P_1(z) = 0$ (oriented isotropically). Red, blue, and black data points represent the surface region, the secondary region below the free surface, and bulk, respectively. (b) Increment of the dielectric dissipation, $\Delta \tan \delta$, at a fixed frequency of $\nu = 1$ kHz resulting from vapor-depositing MTHF (molecular structure is shown in the inset; $T_g = 91$ K) at a constant rate of $R_{\text{dep}} = 0.10$ nm/s onto an interdigitated electrode held at $T_{\text{dep}} = 75$ K. PVD is initiated at $t = 0$ s and terminated at $t = 1,158$ s. The inset shows the reduction of $\Delta \tan \delta$ after the deposition stopped on a logarithmic timescale. The change is shown as percentage of the initial fast rise; the vertical bar in the main frame indicates 100%. This initial fast rise corresponds to a 2.5-nm layer of MTHF with high residual mobility deposited within ~ 25 s. The leveling off near 10^4 s could be a matter of limited system stability. Abbreviations: MTHF, 2-methyltetrahydrofuran; PVD, physical vapor deposition; $P_1(z)$, orientation order parameter. Panel a adapted with permission from Reference 51; copyright 2019 the authors. Panel b adapted with permission from Reference 142; copyright 2020 Royal Society of Chemistry.

and the gradual nature of the change in slope around $t \approx 25$ s suggests a mobility gradient in the PVD glass film. The high values of ΔC and $\Delta \tan \delta$ of this top layer of vapor-deposited MTHF agree with those of bulk MTHF at $T = 94.6$ K. This result suggests that, on average, the dynamics of this top layer are reminiscent of those of bulk MTHF in the SCL state at 94.6 K, where the relaxation time is $\tau_\alpha \approx 0.1$ s. Repeating these measurements at lower deposition temperatures, Thoms et al. also found that the thickness of this mobile layer decreases to ~ 1.2 nm and ~ 0.6 nm at $T_{\text{dep}} = 42$ K and 32 K, respectively.

4.3. Surface-Mediated Aging

Recent in situ dielectric relaxation experiments by Thoms et al. (142) show evidence for enhanced aging rates in the interfacial region. A considerable reduction in $\Delta \tan \delta$ occurs within the first 25 s after the termination of deposition (Figure 8b). The reduction in this loss or dissipation indicates that the packing density is rapidly increased and that a more stable state is achieved in the top 2.5-nm surface layer. Continuing the $\Delta \tan \delta$ measurement for a longer duration reveals a subsequent slow aging process that lasts $\sim 10^4$ s (Figure 8b, inset). This timescale is much shorter than τ_α at the low temperature of $0.82T_g$. We note that the curve in the inset of Figure 8b appears to level off at 20% of the initial raise (fast surface region), suggesting that a mobile layer that is $20\% \times 2.5$ nm = 0.5 nm thick continues to have dynamics much faster than 1 kHz that contribute to the dielectric loss. These observations provide evidence for the existence of both molecular equilibration in the monolayer of the free surface and accelerated aging rates in the interfacial region in the few layers below the mobile surface. Unlike equilibrium relaxations,

aging can result in time-dependent and nonmonotonic properties due to an interplay between the driving force to equilibrium and the effective relaxation times at the aging temperature. Direct measurements of such properties should be conducted to obtain a better understanding of the accelerated rate of aging in the interfacial region.

5. SURFACE-MEDIATED STABLE GLASS FORMATION: FULL PICTURE

Since the discovery of SGs (3), SG formation has been associated with enhanced surface mobility. However, as discussed in this review, building a full picture can be complicated. Ramos et al. (144) speculated that the interactions among molecules that accumulate in a molecule-by-molecule fashion during PVD are stronger than those in LQG, resulting in stability. However, stronger intermolecular interactions lead to a reduced ability to form SGs (51, 81, 85), and measurements in molecules with the same intermolecular interactions show that molecular flexibility can also play a strong role in stability (16) (e.g., **Figures 3** and **6**), challenging this viewpoint. Mangalara et al. (145) proposed that stability upon PVD is a natural consequence of the mismatch between the thermodynamics of the glass interface and bulk and of the resulting dynamical gradients. A T_g lower at the free surface than at the bulk means that the surface also has lower T_f at low temperatures than the bulk glass. As a result, the surface layers of an LQG compared with bulk could also have a higher density, which is then preserved throughout a PVD film. This view is consistent with surface-mediated equilibration in which isotropic SGs are produced, at $T_{\text{dep}} > 0.95T_g$. However, at lower temperatures, where the thickness of the mobile layer is below the molecular size, such equilibrium properties are not observed.

On the basis of the details of the dependence of SG properties on the deposition conditions (see Section 3), we propose a four-layer model of surface-mediated SG formation (**Figure 2**). During PVD, molecules near the free surface possess enhanced surface diffusion, enhanced surface mobility, and lower local T_g compared with the bulk. The local T_g increases with increasing distance from the free surface toward the bulk T_g value. Regions with $T_g(\text{local}) < T_{\text{dep}}$ are at their corresponding equilibrium states. The thickness of this layer decreases with decreasing temperature below T_g (124), causing the equilibrium energy and structure of this layer to vary. Therefore, depending on T_{dep} , the interfacial regions have varying properties, as shown in **Figure 2** for an elongated molecule. At the topmost layer of a PVD film, surface diffusion can be enhanced, and elongated molecules without strong interactions will orient mostly along the free surface. In the next layer, $T_g(\text{local}) < T_{\text{dep}}$ and the molecules can relax and reorient into the local equilibrium configuration. Here, the molecules just below the free surface prefer a vertical orientation, and a PVD film will adopt this orientation if the mobile layer is only two layers thick. If the mobile layer is thicker, the oriented configuration will not persist further into the film and the layer will become isotropic; thus, the resulting PVD glass will not show orientational order. The final orientation of molecules in a vapor-deposited film is therefore defined by the thickness of the layer, with $T_g(\text{local}) < T_{\text{dep}}$. Even deeper into the film, where $T_g(\text{local}) > T_{\text{dep}}$, the molecules are out of equilibrium but may still have enhanced physical aging rates, allowing them to further evolve toward equilibrium and further reducing their energy and increasing their density. Since this accelerated aging process takes place under the constraint of a rigid and immobile layer underneath, the molecules may adjust in a layer-by-layer fashion, thus forming tighter out-of-plane distancing (layering). Finally, after experiencing these three phases, the molecules are arrested in a steady out-of-equilibrium state with structure and stability that are dictated by a combination of the properties gained in the three interfacial regions.

Figure 9 illustrates how deposition at various T_{dep} values can affect the anisotropy and stability of PVD glasses of a rigid, elongated molecule. When vapor deposition is performed above $T_g(\text{bulk})$ (**Figure 9e**), most of the film is at equilibrium, independent of R_{dep} . Therefore, the horizontal

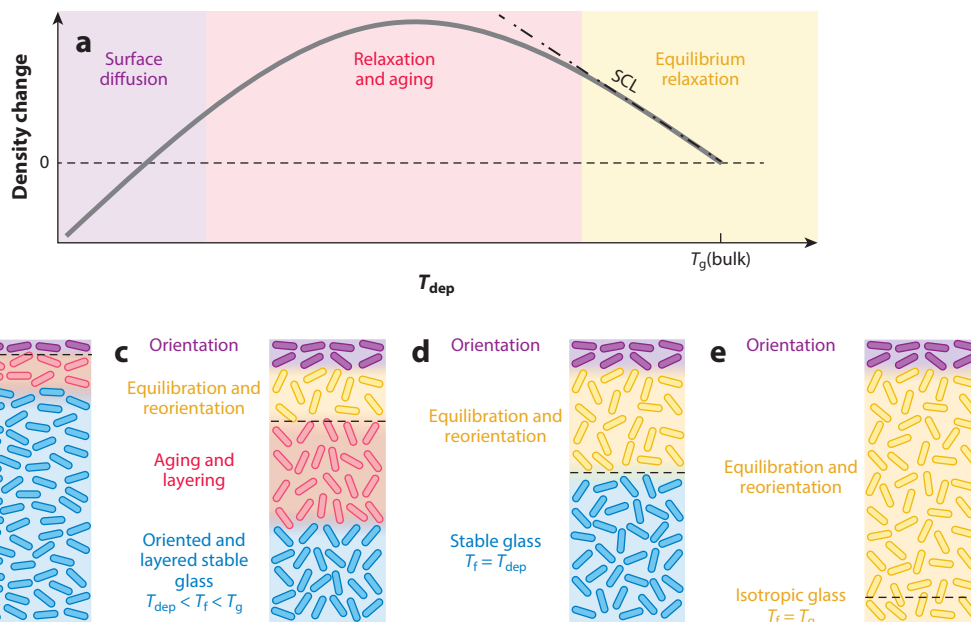


Figure 9

Schematic illustration of dynamical processes at play during surface-mediated SG formation at different T_{dep} values. (a) A representative sketch of the density change versus T_{dep} at a constant R_{dep} . The dash-dotted line represents the extrapolated density of the SCL. The color-coded regions correspond to deposition regimes where the glass structure is influenced by surface diffusion (purple), relaxation and aging (pink), and equilibrium relaxation (yellow). (b–e) The lozenge shapes represent the orientation of nonspheroidal molecules, and each dashed line denotes the position where $T_g(\text{local}) = T_{\text{dep}}$. The location of this line also depends on the surface equilibration time (inversely proportional to R_{dep}). (b) At low T_{dep} , only the topmost layer has enhanced lateral surface diffusion, which is not sufficient to produce highly stable glasses. PVD glasses with low stability produced in this region have pronounced in-plane orientation. (c) At intermediate T_{dep} , the mobile surface is a few layers thick, allowing partial equilibration. PVD in this region produces kinetically trapped SGs with partially enhanced stability and orientations, the degree of which depends on the thickness of the mobile layer—isotropic, out of plane, or in plane as T_{dep} is decreased. Since that equilibrium is not achieved in this regime, layered packing can also be observed if the interfacial aging rate is significantly enhanced. (d) Near T_g , the thickness of the mobile surface layer is such that its equilibrium conditions are the same as the corresponding bulk SCL and its mobility is enhanced such that equilibrium is achieved during deposition. As such, no further aging is possible. Deposition in this regime produces isotropic glasses with the same density as the bulk SCL (i.e., $T_f = T_{\text{dep}}$). (e) Deposition above $T_g(\text{bulk})$ produces glasses with isotropic molecular packing and the same stability as the LQG because the glass is in the SCL state during deposition. Abbreviations: LQG, liquid-quenched glass; PVD, physical vapor deposition; SCL, supercooled liquid; SG, stable glass.

orientation of the molecules at the air–liquid interface does not affect the PVD glass properties, as molecules reorient and equilibrate into an isotropic packing once buried deep into the film. The resulting glass has the same properties as the LQG with $T_f = T_g$. Just below $T_g(\text{bulk})$ (Figure 9d), the molecules right below the free surface still have enough mobility to reach their local equilibrium [$T_g(\text{local}) < T_{\text{dep}}$], and the liquidlike surface is thick enough to produce the same isotropic equilibrium state as the bulk SCL. The resulting PVD glasses, typically deposited at $0.95T_g < T_{\text{dep}} < T_g$, are thus isotropic and have the same density as the extrapolated bulk SCL (i.e., $T_f = T_{\text{dep}}$). Given that equilibrium is achieved in this layer, there is no further aging; therefore, one does not expect to see layering structures in this region. We note that the effective rate of equilibration during PVD is much faster than bulk aging rates, indicating significantly enhanced mobility.

As T_{dep} is reduced further, the thickness of the equilibrium surface region decreases (124) and stronger mobility gradients and mobility anisotropy emerge (16). When PVD is performed in the

intermediate range (typically $0.75T_g < T_{\text{dep}} < 0.95T_g$), the resulting properties strongly depend on the chemical structure of the molecules (e.g., **Figure 3**). For a hypothetical lozenge-shaped molecule, in this deposition range (**Figure 9c**) the region becomes thin enough that the local equilibrium structure can have preferred orientations ranging from isotropic to out of plane to in plane as the layer thickness reduces upon decreasing T_{dep} . Furthermore, the equilibrium surface state can have higher energy and lower density than the bulk SCL, thus preventing full equilibration of the PVD glass. As the molecules sink further into the film and fall out of equilibrium below the layer with $T_g(\text{local}) = T_{\text{dep}}$, they still have a thermodynamic driving force to age toward the bulk SCL state. If they experience sufficiently enhanced mobility, for example, at low R_{dep} , they can further age toward equilibrium. Therefore, a partially equilibrated SG is produced with $T_{\text{dep}} < T_f < T_g$, a lower density than that of the corresponding SCL. The structure of this glass can show both layering and orientational anisotropy, the degree of which is defined by T_{dep} and R_{dep} as well as by the chemical structure. When deposition is performed at very low T_{dep} (**Figure 9b**), surface mobility is not high enough to allow for equilibration and reorientation underneath the topmost layer. The air–liquid interface will impose an in-plane orientation that is mostly maintained as deposition continues. While the thermodynamic driving force to equilibration increases with decreasing T_{dep} , the degree of accelerated aging in this region also drops rapidly due to the overall slower dynamics, decreasing mobility gradients, and decreasing thickness of the layer with accelerated aging (e.g., **Figures 3c** and **6c**). As a result, the degree of stability as well as layering rapidly decreases for most molecules in this deposition region, eventually leading to the formation of unstable glasses at very low T_{dep} ($T_f \geq T_g$).

The specific T_{dep} range for each region also depends on the deposition rate, R_{dep} , through the RTS relationship (Section 3.2), indicating the temperature dependence of the effective surface relaxation time (53) (**Figure 7c**). In addition, molecular-specific effects can affect the details of each deposition regime. In spherically shaped molecules, such as Alq3 (9) and α , α -A (16), there is no preferred orientation at the free surface. In rigid molecules, the temperature range of mobility anisotropy and the range of mobility gradients are enhanced at low temperatures (16), resulting in a broader range of temperatures where SGs are formed, such as in α , α -A (**Figure 3a**) and its simulated counterpart (**Figure 6**). In contrast, in strongly interacting molecules, the window of T_{dep} values in which SGs can form shrinks (85). Lastly, specific chemical motifs can segregate to the free surface, which can result in an out-of-plane orientation (51) and slightly change the picture presented in **Figure 9**.

6. SUMMARY AND FUTURE OUTLOOK

While the existing evidence for the process of surface-mediated SG formation is convincing, many of the details of surface mobility enhancement and the resulting mobility gradients remain underexplored. Experiments and simulations in both PVD and LQG thin films indicate that the thickness and dynamics of the mobile surface layer are influenced by both the free surface and the glass layer underneath, through kinetic facilitation (16, 96, 97, 101). In addition, there is some evidence for further out-of-equilibrium aging in the interfacial region, the details of which remain poorly understood. The surface-mediated enhanced aging rate and kinetic facilitation effects generate nontrivial effects in which measurements of the LQG surface may not be adequate to fully predict the mobility profiles on the SG surface. Surprisingly, under some conditions, the SG surface may have greater mobility than the LQG surface (16). These observations can explain why moderately enhanced free surface mobility on LQG surfaces can sometimes translate into orders-of-magnitude enhancement in stability during PVD. Moreover, the origins of enhanced mobility are not clear, as most theoretical studies predict mobility profiles that are more or less predicted

by the equilibrium glass structure (63, 65, 116) and, thus, should not be affected by the degree of stability. Understanding this physics may elucidate missing details in our understanding of glass physics in general. As such, it is imperative to develop new experimental methods and extend the range of timescales in simulations to investigate mobility profiles on various surfaces. Development of in situ characterization techniques (142) can also help elucidate the interplay between aging and equilibration as a PVD film grows. In situ measurements of dielectric relaxation over a broader range of molecules and deposition conditions can verify whether accelerated aging occurs at the free surface and estimate its effective aging rate. Experiments containing probe molecules at various depths could help distinguish equilibrium relaxations and aging dynamics as well as their roles in stability.

Another promising technique is to implement in situ grazing-incidence X-ray photon correlation spectroscopy measurements during PVD to monitor the interfacial microscopic relaxation dynamics on timescales ranging from microseconds to thousands of seconds (146). Since molecular flexibility and shape appear to significantly alter surface mobility profiles (16), further studies of the structure–property relationship in glass-forming isomers with precise variations in their chemical and structural properties are warranted; they can then be combined with machine learning approaches to gain further insight in order to control mobility profiles. External factors such as light illumination (50) or postdeposition cross-linking can also be used to control properties. Whether these abundant structural features observed in stable molecular glasses are universal in other systems, such as metallic, polymeric, and oxide glasses, upon PVD is also important for understanding the origin of enhanced surface mobility and its role in SG formation. These studies could lead to a predictive understanding of the structure–property relationships in glass-forming materials in general. Further studies in these systems could also lead to the development of broader strategies to control mobility and PVD glass structure and to utilize them in a wider range of applications.

While this review has focused on the properties of steady-state bulk PVD glasses, there is significant evidence that thin films' properties may be distinctly different (69). Thin films of both LQGs (69, 147, 148) and PVD glasses (69) show nontrivial density variations and exceptionally high density values. For example, we have observed up to 8% higher density in PVD thin films of TPD, exceeding bulk SCL and crystal density (69). These variations in thin-film properties are due to the strong dependence of mobility profiles on the film thickness and the substrate boundary conditions, in addition to the free surface (97, 100). In LQG thin films, enhanced mobility results in more homogeneous properties and liquidlike behavior (e.g., **Figure 7b**) (89, 96). During PVD, this additional mobility enhancement as well as inherent changes in the thin-film equilibrium liquid structure can provide access to previously unknown phases with a liquid–liquid phase transition well below bulk T_g (69). These dramatic property changes can enable the production of new materials and elucidate hidden phase transitions that are not otherwise observed in LQGs. Aside from deposition rate and temperature, other strategies that could generate more dimensions for controlling thin-film properties deserve further exploration. For example, while substrate effects do not strongly influence the properties of bulk PVD glasses, deposition on substrates with various properties can produce glasses with different structures and properties in thin films.

In summary, we have reviewed existing data that explore the properties of SCL surfaces and demonstrated that, compared with bulk, glass surfaces exhibit enhanced diffusion and relaxation as well as mobility anisotropy. The air–liquid boundary conditions also lead to preferred orientations, segregation of chemical motifs, and density changes in the interfacial region. These effects provide an exquisite ability to access hidden regions of the energy landscape to produce exceptionally stable glasses. The properties of these glasses and their degree of stability can be tailored by tuning the deposition parameters, chemical modifications, film thickness, and external stimuli such as light.

These studies motivate further direct and indirect measurements of surface mobility profiles on molecular, metallic, polymeric, and oxide glasses to understand the origin of these phenomena, and they offer an opportunity to develop a predictive understanding of the structure–property relationships in glass-forming materials.

DISCLOSURE STATEMENT

The authors are not aware of any affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

ACKNOWLEDGMENTS

We thank Dr. Yitao Sun for help with schematic drawings and Dr. Sarah E. Wolf, Dr. Richard Stephens, and Kritika Jha for helpful discussions. We acknowledge financial support from the National Science Foundation (NSF) under grant DMREF-1628407 and the NSF Materials Research Science and Engineering Centers under grant DMR-1720530. P.L. acknowledges postdoctoral fellowship funding from the School of Arts and Sciences of the University of Pennsylvania.

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