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# Surface mobility of molecular glasses and its importance in physical stability☆

Lian Yu

*University of Wisconsin-Madison, School of Pharmacy and Department of Chemistry, United States*

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ABSTRACT

Amorphous molecular materials (molecular glasses) are useful for drug delivery, bio-preservation and organic electronics. A central issue in developing amorphous materials is the stability against crystallization and other transformations that can compromise material performance. We review recent progress in understanding the stability of molecular glasses, particularly the role for surface mobility. Surface diffusion in molecular glasses can be vastly faster than bulk diffusion. This high surface mobility enables fast crystal growth on the free surface. In this process, surface crystals grow upward and laterally, with the lateral growth rate being roughly proportional to surface diffusivity. Surface mobility also influences bulk crystal growth as the process can create fracture and free surfaces. During vapor deposition, surface mobility allows efficient equilibration of newly deposited molecules, producing low-energy, high-density glasses that are equivalent to liquid-cooled glasses aged for thousands of years. Free surfaces can accelerate chemical degradation of proteins. Measures for inhibiting surface-facilitated transformations include minimizing free surfaces, applying surface coatings, and preventing fracture.

## 1. Introduction

Glasses are amorphous materials that combine the mechanical strength of crystals and the spatial uniformity of liquids. Compared to crystals, glasses are more easily fabricated to be spatially homogeneous from macroscopic to nearly molecular dimensions. Such spatial uniformity is the basis for their wide applications in optics and contributes to the superior strength of metallic glasses [1,2]. While better-known glasses are inorganic and polymeric, organic glasses of relatively low molecular weights ("molecular glasses") are being explored for applications in drug delivery [3,4,5], bio-preservation [6,7], and organic electronics [8,9]. Pharmaceutical scientists take advantage of the high solubility of amorphous solids for the delivery of poorly soluble drugs.

An important subject in the study of molecular glasses is physical stability [5,10,11]. Glasses are non-equilibrium solids formed by cooling liquids, condensing vapors, or evaporating solutions while avoiding crystallization. A common feature of these processes is the kinetic arrest of a fluid structure. In glass formation by liquid cooling (Fig. 1), molecular motions slow down with falling temperature and eventually the system falls out of equilibrium at the so-called glass transition temperature $T_g$, forming a solid glass. Glasses are thermodynamically driven to crystallize and to "age" toward the equilibrium liquid state, both processes leading to changes in structure, properties, and performance.

A recent progress in understanding glass stability is the finding that molecular glasses have extremely high surface mobility and this property causes problems of poor stability and paradoxically, provides a tool for preparing glasses with vastly improved stability. Here we discuss this recent progress. Section 2 reviews recent measurements of surface diffusion on molecular glasses. Section 3 discusses the role of surface mobility in the physical stability of molecular glasses. We show that surface mobility is directly responsible for fast crystal growth on free surfaces, and may be involved in bulk crystal growth through the creation of voids and free surfaces. In vapor deposition, surface mobility allows efficient equilibration of newly deposited molecules and the formation of stable glasses with exceptionally low energy and high density. We also consider the methods for stabilizing molecular glasses against surface-facilitated transformations.

## 2. Surface mobility of molecular glasses

Recent experiments have shown that molecules on the free surface of an organic glass can be much more mobile than those in bulk. The experiments that led to this conclusion include the evolution of surface contours driven by surface tension [12,13,14,15,16], the conductivity of ions implanted at different depths [17], the embedding of nanoparticles [18], and the rotation of probe molecules [19]. The high mobility of surface molecules is qualitatively understood from their special environment: a surface molecule has fewer neighbors than a bulk molecule and a greater freedom of movement.

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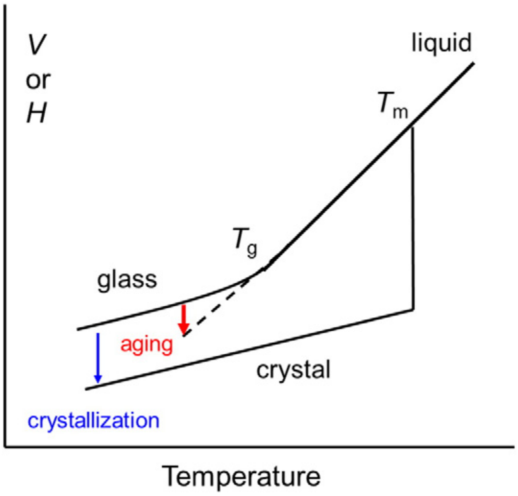

**Fig. 1.** Formation, crystallization and aging of glasses. Cooling a liquid without crystallization produces a glass below $T_g$ (the glass transition temperature). $V$ is volume; $H$ is enthalpy. A glass is driven to crystallize and age toward the supercooled liquid.

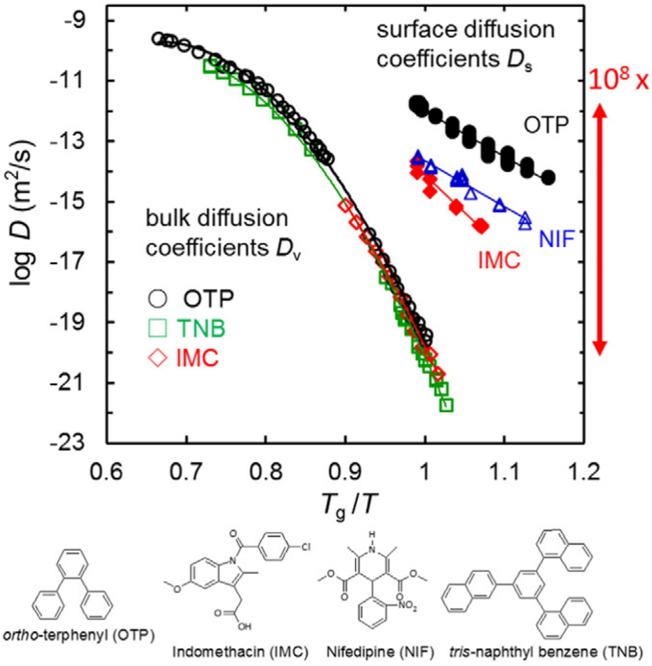

**Fig. 2.** Surface and bulk diffusion coefficients ($D_s$ and $D_v$) vs. $T_g/T$. Note that $D_s$ can be $10^8$ times larger than $D_v$ at $T_g$. The $D_v$ values are clustered while the $D_s$ values show stronger molecular dependence.

Diffusion can be vastly faster on the free surface of a molecular glass than in the interior [ 12,13,14]. Here, surface diffusion refers to the lateral translation of surface molecules. Fig. 2 compares the coefficients of surface diffusion and bulk diffusion, $D_s$ and $D_v$, for several systems. The temperature is scaled by $T_g$, which allows the $D_v$ values of different systems to approximately collapse to one master curve, serving as a reference for comparing surface diffusivity. For the three systems in Fig. 2, indomethacin (IMC), Nifedipine (NIF), and *o*-terphenyl (OTP), $D_s/D_v$ is $10^6$ to $10^8$ at $T_g$ and the ratio increases with cooling, since $D_v$ decreases faster than $D_s$. The fast surface diffusion suggests the importance of surface-facilitated processes, as we discuss later.

The results in Fig. 2 indicate that if the different systems are compared at the same bulk diffusivity, surface diffusion slows down as intermolecular forces increase. At the same $D_v$, surface diffusion follows the order OTP > NIF > IMC, or the opposite order for intermolecular forces. To see this, note that OTP is the smallest molecule and forms no hydrogen bonds. NIF and IMC are similar in size and IMC forms stronger hydrogen bonds (for its carboxyl group) than NIF. The physical picture is that the small, loosely bound OTP molecules are freer to diffuse on the surface than the larger, more strongly bound NIF and IMC molecules. In very recent work, this picture was extended to include low-molecular-weight polymers [20]. The surface diffusion of polystyrene oligomers ($M_w = 1$–$2$ kg/mol) is significantly slower than that of the small molecules, with $D_s/D_v \approx 10^5$ at $T_g$, and has a higher activation energy. This effect is attributed to a steep mobility gradient beneath the surface and deeper penetration of polymer chains into the bulk. The molecular dependence of surface mobility suggests that surface-facilitated processes have system-dependent rates.

The surface diffusion coefficients in Fig. 2 were obtained by the method of surface-grating decay [21]. For molecular glasses, a sinusoidal grating pattern was embossed onto a free surface and its flattening was observed over time under the driving force of surface tension [12,13,14]. While the flattening can occur by several mechanisms, surface diffusion dominates at short wavelengths. Mullins showed how the wavelength dependence of the decay rate $K$ can be used to determine the mechanism of surface evolution [21]; for example, $K \propto \lambda^{-4}$ is the signature of surface diffusion and $K \propto \lambda^{-1}$ is the signature of viscous flow (collective motion of a liquid in a pressure gradient). While Mullins's method to measure surface diffusion was first applied to crystalline metals and silicon, simulations have shown that the method yields accurate surface diffusivity for glasses [22].

A common feature for all the molecular glass-formers studied to date (Fig. 2) [12,13,14] is that the mechanism of surface evolution changes from viscous flow at high temperatures to surface diffusion at low temperatures. The viscosity at which this transition occurs $\eta_t$ depends on the rate of surface diffusion: slower surface diffusion allows viscous flow to control surface evolution up to a higher viscosity. Thus, $\eta_t$ can be used to compare the surface diffusivity of different materials. For example, at $\lambda = 1000$ nm, $\eta_t = 10^6$–$10^8$ Pa s for the small-molecule glasses in Fig. 2, and $>10^{10}$ Pa s for polystyrenes, consistent with the latter's slower surface diffusion [14,20].

Computer simulations have observed faster molecular rotation at the surface of a free-standing OTP film [23] and faster diffusion at the surface of a glass-forming binary Lennard–Jones liquid [22,24]. At present, the lowest temperature accessible to simulations is still far above the laboratory $T_g$. For the binary LJ system, surface diffusion is $10^3$ times faster than bulk diffusion, $D_s/D_v = 10^3$, when $D_v = 10^{-13}$ m$^2$/s [22]. Similar result was obtained for the metallic glass ZrNi [25]. This enhancement ratio is consistent with the ratio for OTP and IMC, if we extrapolate the data in Fig. 2 to high temperatures. This agreement suggests that the LJ model could capture the essential feature of surface mobility for van der Waals and metallic systems. For the LJ system, the transition from surface mobility to bulk mobility takes place over a distance of several particle diameters [22,24].

Two equations have been proposed to predict the degree to which mobility is enhanced at a glass surface: [26,27].

$$\tau_\alpha/\tau_{surf} = (\tau_\alpha/\tau_0)^{0.5} \tag{1}$$

$$\tau_\alpha/\tau_{surf} = (\tau_\alpha/t_c)^{n} \tag{2}$$

In these equations, $\tau_\alpha$ and $\tau_{\text{surf}}$ are the bulk and surface relaxation times respectively. Eq. (1) originates from the Random First Order Transition (RFOT) theory, with $\tau_0 \approx 1$ ps [26], and Eq. (2) from the Coupling Model (CM), where $t_c \approx 2$ ps and $n$ is obtained from the Kohlrausch–Williams–Watt (KWW) exponent for fitting the bulk relaxation kinetics: $\Phi = \exp.[-(t/\tau_\alpha)^{1-n}]$ [27]. Both equations predict that surface mobility can be vastly higher than bulk mobility and have a weaker temperature dependence—features that also characterize surface diffusion on molecular glasses (Fig. 2). A key difference between the two models is that Eq. (1) predicts a universal relation between $\tau_\alpha/\tau_{\text{surf}}$ and $\tau_\alpha$, whereas Eq. (2) predicts a material-dependent one.