

## Stable Glass Transformation to Supercooled Liquid via Surface-Initiated Growth Front

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Highly stable glasses of tris-naphthylbenzene transform into a liquid when annealed above the glass transition temperature  $T_g$ . In contrast to the predictions of standard models, the observed transformation is spatially inhomogeneous. Secondary ion mass spectrometry experiments on isotopically labeled multilayer films show that the liquid grows into the stable glass with sharp growth fronts initiated at the free surface and at the interface with the substrate. For the free surface, the growth velocity is constant in time and has the same temperature dependence as self-diffusion in the equilibrium supercooled liquid. These stable glasses are packed so efficiently that surfaces and interfaces are required to initiate the transformation to the liquid even well above  $T_g$ .

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Glassy materials lack long-range translational order, but can still exhibit a strong resistance to deformation. This property is central to many applications and, as a result, the mechanism by which amorphous materials lose their rigidity by transforming into liquids upon heating has been extensively investigated. Essentially all previous work and all the common models that describe this process share a common viewpoint: the transformation of a glass to a liquid upon heating is spatially homogeneous, i.e., it occurs in the same manner throughout the sample and is independent of the sample size. In this view, upon annealing above the glass transition temperature  $T_g$ , molecules throughout the system are simultaneously released from their glassy environments and begin to sample the variety of local packing arrangements characteristic of the liquid at the annealing temperature.

Here we report that the transformation of a glass to a liquid can occur in a spatially inhomogeneous manner, as a growth front initiated at the sample surface. While the traditional homogeneous description may be reasonable for glasses prepared by cooling a liquid at a typical laboratory rate, it does not describe highly stable glasses that are much lower on the energy landscape. The molecules in highly stable glasses are efficiently packed into such low energy arrangements that long annealing above  $T_g$  is not sufficient to release a typical molecule from the glassy state. Rather, growth of the liquid state is initiated at the surfaces of the sample and only those glass molecules at the glass-liquid interface can be transformed into the liquid. Here the growth front initiated at the free surface is observed to propagate into the glass at constant velocity. These results not only describe a previously unreported aspect of the glass transition, but they may provide insight into the interactions that occur in supercooled liquids

between much smaller regions with different mobilities, i.e., dynamic heterogeneity [1,2], as we discuss below.

For these experiments, isotopically labeled multilayer thin film glasses of tris-naphthylbenzene (TNB) were prepared by physical vapor deposition. We have recently shown that vapor deposition can produce high density, low enthalpy, extraordinarily stable TNB glasses if the substrate temperature and deposition rate are carefully controlled [3]. In this work, protio-TNB (h-TNB;  $C_{36}H_{24}$ ) [4] and deuterio-TNB (d-TNB;  $C_{36}H_{10}D_{14}$ ) [5] were alternately deposited onto a silicon wafer with a thick oxide coating. Glasses similar to those obtained by cooling liquid TNB at typical laboratory rates (“ordinary glasses”) were prepared by vapor deposition onto wafers at 340 K while highly stable glasses were produced when the substrate was held at 295 K [6]; in all cases, the deposition rate was  $0.1 \pm 0.05$  nm/s. After deposition, small pieces of each wafer were annealed at various temperatures near  $T_g = 347$  K. The h-TNB and d-TNB concentration profiles of these thin film samples were measured after annealing by secondary ion mass spectrometry (SIMS), as described elsewhere [7], with spatial resolution of  $\sim 5$  nm.

Figure 1 illustrates that the evolution of the isotope concentration profile in an ordinary TNB glass (vapor deposition at 340 K) occurs uniformly throughout the sample upon annealing near  $T_g$ . The top curve illustrates the d-TNB concentration profile of the as-deposited sample. The three lower curves show the evolution of this concentration profile due to annealing at the indicated temperatures. The gray (red) lines are fits to the Fickian diffusion model; for each curve, the as-deposited profile is used as the starting condition and the single fitting parameter is the diffusion coefficient  $D$  [7]. Elsewhere we show that a single diffusion coefficient can simultaneously de-

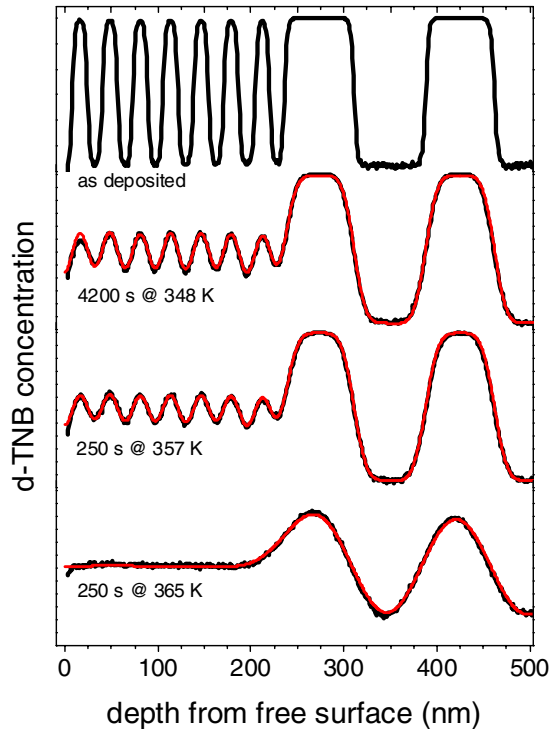


FIG. 1 (color online). Homogeneous evolution of ordinary glass upon annealing near  $T_g$ . Alternating vapor deposition of h-TNB and d-TNB at 340 K produces the d-TNB concentration profile shown at the top, as measured by SIMS. Thick (black) lines are concentration profiles after annealing as indicated. Thin [gray (red)] lines are predictions of the Fickian diffusion model with  $D = 1.0 \times 10^{-16} \text{ cm}^2/\text{s}$  at 348 K,  $2.0 \times 10^{-15} \text{ cm}^2/\text{s}$  at 357 K, and  $D = 3.2 \times 10^{-14} \text{ cm}^2/\text{s}$  at 365 K.

scribe multiple annealing times at a given temperature, and that  $D$  is independent of initial sample profile and total film thickness throughout the temperature range from 338 to 365 K [7]. Thus the evolution of an ordinary glass, upon annealing near  $T_g$ , shows no induction time and occurs homogeneously throughout the sample (as viewed by the SIMS experiment).

In contrast, Fig. 2 demonstrates that stable TNB glasses (vapor deposition at 295 K) evolve inhomogeneously upon annealing near  $T_g$ . The d-TNB concentration profile in the middle of the film remains unchanged even after very long annealing times at 345 K. Modified concentration profiles are seen at the edges of the film, and these changes propagate into the center of the film over time. A sharp growth front originates at both the free surface and the interface with the substrate, giving rise to material that has much higher mobility than the stable glass. Prior to passage of the front, the stable glass shows no molecular motion on the length scales probed by SIMS. The sharp central features in the bottom panel of Fig. 2, for example, have not broadened after nearly one day at 345 K, indicating that  $D \leq 10^{-18} \text{ cm}^2/\text{s}$  in the stable glass; this is at least 30 times lower than the value for the supercooled liquid at this

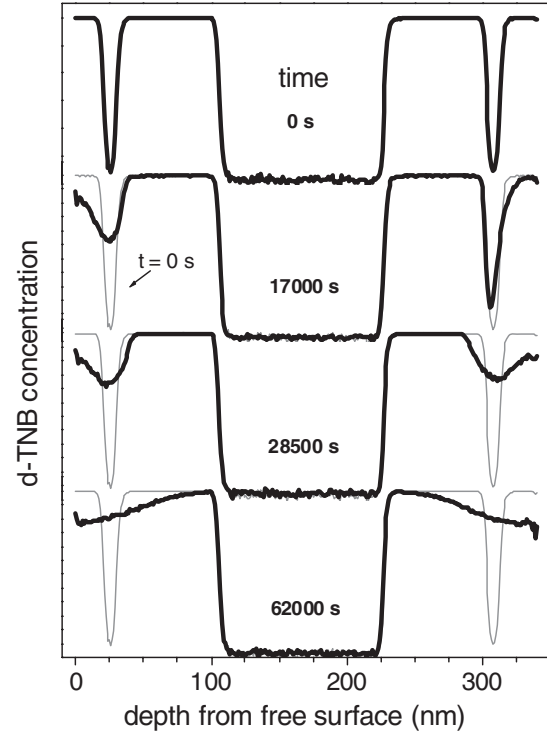


FIG. 2. Spatially inhomogeneous evolution of stable TNB glasses (vapor deposited at 295 K) upon annealing at 345 K. Alternating vapor deposition of h-TNB and d-TNB produces the d-TNB concentration profile shown in the top curve. Growth fronts move into the sample from the free surface and from the substrate interface. The initial concentration profile is superposed with profiles after annealing to illustrate where the growth front is located.

temperature [7]. Previous neutron reflectivity measurements on stable glasses, with higher spatial resolution than these SIMS measurements, indicate that  $D \leq 10^{-19} \text{ cm}^2/\text{s}$  at 345 K in the stable glass [8].

The growth front that transforms stable TNB glass into a liquid moves into the sample from the free surface with a constant velocity and no induction time, as shown in Fig. 3. Here we collect data from seven different samples annealed at 345 K, with most of these samples annealed for two or three different times. The position of the growth front after annealing was identified visually by comparison with the initial concentration profile, as illustrated in Fig. 2. While the growth fronts apparent in Fig. 2 would not be visible in a SIMS measurement without isotopic labeling, the multilayer construction of our samples does not influence the transformation of the stable glass to a liquid. Figure 3 includes data from films in which both the total thickness and the layer thicknesses were varied. No systematic dependence on initial film structure or thickness is observed.

To our knowledge, there is no precedent for our observation of glass transforming into liquid via a growth mechanism. By far the most common description of the

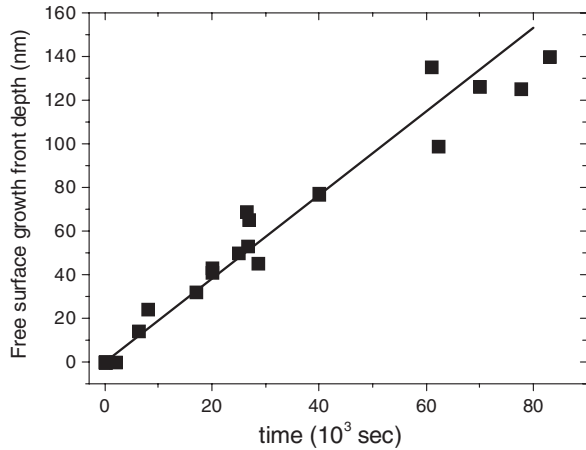


FIG. 3. Position of the mobility growth front, measured from the free surface of stable TNB glasses, as a function of annealing time at 345 K. The solid line is a linear fit with zero intercept, with the slope equal to the growth velocity  $V_{gr} = 0.0019$  nm/s. All these stable glass samples were deposited at 295 K.

glass to liquid transformation is the model devised by Tool, Narayanaswamy, and Moynihan (TNM) [9–11]. In this approach, the relaxation time near  $T_g$  depends upon both the temperature  $T$  and the instantaneous structure of the material. The latter is characterized by the fictive temperature  $T_f$ . As neither  $T$  nor  $T_f$  depend upon spatial position in the TNM model, this is a spatially homogeneous description and the transformation to the liquid is predicted to occur everywhere simultaneously. While the TNM approach has enjoyed reasonable success in describing organic and inorganic glass formers [12,13], it clearly lacks the correct physics to describe the observed growth mechanism for the transformation of a stable glass to a liquid.

We explain the unprecedented nature of our observations by noting that glasses produced by vapor deposition can be much more stable than ordinary glasses that have been aged for long times below  $T_g$  [3,14]. An ordinary glass, prepared by cooling a liquid at a few K/min, is formed when molecular relaxation times become large in comparison to the time scale associated with cooling. Since glasses are out of equilibrium, aging for long periods of time below  $T_g$  does result in further stabilization, but this process occurs very slowly. When an aged glass is annealed above  $T_g$ , the transformation to the supercooled liquid can be significantly delayed. For example, Kovacs aged poly(vinyl acetate) below  $T_g$  for two months and then jumped the temperature to just above  $T_g$  [15]. The volume of the system responded sluggishly, requiring  $\sim 30\tau_\alpha$  to equilibrate, where  $\tau_\alpha$  is the structural relaxation time at the final temperature. In comparison, the sharp central feature in the stable TNB glass in Fig. 2 shows no indication of relaxation after more than  $600\tau_\alpha$  [16,17]. Based on other measures of glass stability, including density and enthalpy, we have estimated that an ordinary TNB glass would have to

be aged for more than 1000 years to reach the stability of the vapor-deposited samples used here [14].

The essential features of Figs. 1–3 are easily understood at a semiquantitative level. Vapor-deposited stable glasses have low enthalpies and high densities. Molecular packing in these systems is highly efficient. Even though there is a thermodynamic driving force for transformation to the liquid, packing is so tight that molecules are kinetically trapped by their glassy neighbors even after extensive annealing above  $T_g$ . For these TNB samples, surfaces and interfaces initiate the transformation to the liquid. Once a region of liquid exists, the liquid grows as individual molecules (or small clusters) are freed from the stable glass. This process establishes a sharp growth front, and if the growth front is planar, the propagation velocity should be constant since all relevant forces are short range. In thicker samples, we speculate that structural defects in the interior of the sample can initiate growth fronts that propagate into the surrounding stable glass.

Figure 4 tests one feature of the above explanation. Growth velocity measurements, like those shown in Fig. 3, have been performed at two other annealing temperatures. These measurements are compared in Fig. 4 to the temperature dependence of the self-diffusion coefficient for supercooled TNB [7]. The good agreement between the two temperature dependences is consistent with a mechanism in which molecular rearrangements in the liquid are the rate-limiting step for extracting a molecule from the stable glass. At all three temperatures, the time required to transform one monolayer of TNB stable glass into liquid is similar to the time required to diffuse one molecular diameter in the liquid. Also shown as an open circle in Fig. 4 is the growth front velocity calculated from neutron reflectivity

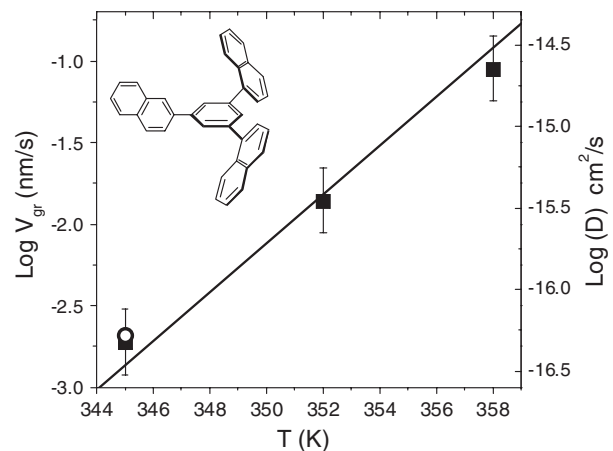


FIG. 4. Mobility growth front velocity  $V_{gr}$  versus annealing temperature for the free surface of stable TNB glasses. Solid squares are SIMS measurements, and the open circle is from neutron reflectivity data [18]. All samples were deposited at 295 K. Solid line is the diffusion coefficient for the equilibrium supercooled liquid [7]. A low energy conformation of TNB is shown in the inset.

tivity experiments on similarly prepared stable TNB glasses [8,18]. While it was not possible to establish in that work that growth fronts propagate from the surfaces, those data yield a growth rate in good agreement with the SIMS data if interpreted in this manner.

It is possible that the stable glass should be envisioned as a distinct amorphous phase [19,20] and that the observed growth front might represent a first order phase transition [19]. The current experiments cannot distinguish between this scenario and the one presented in the previous paragraph.

In these experiments on stable TNB glasses, the free-surface initiates growth of the liquid. This is reasonable given evidence that glass surfaces can be much more mobile than the bulk glass [21–24]. In addition, the formation of stable glasses by vapor deposition requires the existence of a liquidlike layer at the surface; the configurational sampling that occurs in this layer during deposition allows low energy, high density glasses to be formed when the substrate temperature is near  $0.85T_g$  [3,6,14]. Thus we envision that a preexisting liquid layer at the free surface provides a plane of sites that initiate growth of the liquid into the stable glass. Upon annealing, this growth occurs steadily with no induction time.

Two features of the experimental results are more complex and will be discussed in detail elsewhere. It is apparent in Fig. 2 that a growth front is also initiated at the substrate interface. This front sometimes moved at the same velocity as the free-surface front and sometimes moved faster. We do not understand this variability, but it is clear that the growth fronts at both film interfaces are similar surface-initiated processes. We have explored different substrate chemistries, such as metal or polymer coatings, but these do not play a role in the observed behavior. We expect that the growth velocities measured from the top and bottom of the film will become equal at steady state, and some preliminary results support this view. We emphasize that substrate treatment had no influence on the growth observed from the free surface. A second complex feature is the mixing of h-TNB and d-TNB on the liquid side of the growth front. We attempted to model this behavior using the supercooled liquid diffusion coefficients [7], but the mixing observed is consistently faster by a factor of 2–3. Either an additional mechanism beyond diffusion contributes or the liquid formed by the growth front is subtly different than the equilibrium supercooled liquid.

In the past 15 years, it has become clear that dynamics in supercooled liquids are spatially heterogeneous [1,2], and this work provides a useful lens through which we view these new results on the transformation kinetics of stable glasses. In a supercooled liquid, spontaneous fluctuations cause different regions of the sample to transiently expe-

rience different relaxation times; regions only a few nanometers apart can relax at rates that differ by more than a factor of 100. We draw an analogy between these dynamically heterogeneous regions and the inhomogeneous growth kinetics discussed here. On the scale of a few nanometers, a slow region transforming into a fast region might be quite similar for these two situations. In each case, perhaps a few molecules at a time are transformed from “slow” to “fast.” Thus, the growth front kinetics described here may provide critical information needed to understand the interaction between regions of different dynamics that occur in many supercooled liquids and glasses, such as the exchange times required to transform from a slow to a fast region [25].

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