Hiking down the Energy Landscape: Progress Toward the Kauzmann Temperature via Vapor Deposition

Kenneth L. Kearns, Stephen F. Swallen, and M. D. Ediger*
Department of Chemistry, University of Wisconsin—Madison, Madison, Wisconsin, 53706

Tian Wu,† Ye Sun, and Lian Yu
School of Pharmacy, University of Wisconsin—Madison, Madison, Wisconsin, 53705

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Physical vapor deposition was employed to prepare amorphous samples of indomethacin and 1,3,5-(tris)-naphthylbenzene. By depositing onto substrates held somewhat below the glass transition temperature and varying the deposition rate from 15 to 0.2 nm/s, glasses with low enthalpies and exceptional kinetic stability were prepared. Glasses with fictive temperatures that are as much as 40 K lower than those prepared by cooling the liquid can be made by vapor deposition. As compared to an ordinary glass, the most stable vapor-deposited samples moved about 40% toward the bottom of the potential energy landscape for amorphous materials. These results support the hypothesis that enhanced surface mobility allows stable glass formation by vapor deposition. A comparison of the enthalpy content of vapor-deposited glasses with aged glasses was used to evaluate the difference between bulk and surface dynamics for indomethacin; the dynamics in the top few nanometers of the glass are about 7 orders of magnitude faster than those in the bulk at $T_g - 20$ K.

Introduction

Glasses are an important class of materials. They exhibit many of the mechanical properties of crystalline solids while maintaining the disordered microscopic structure of a liquid. Glasses can be made from organic, inorganic, and metallic systems using an array of techniques including physical vapor deposition and slow cooling from the liquid. This wide breadth of materials and techniques translates into a large number of applications for glasses. For example, amorphous silicon is important for photovoltaic applications; vitreous silica is the material of choice for optical fibers; glassy polymers are heavily utilized for optical and structural applications.

One fundamental issue that remains unresolved for amorphous materials is the Kauzmann entropy crisis. Figure 1 is a schematic that illustrates the central issue. If crystallization can be avoided as a liquid is cooled below the melting temperature $T_m$, the liquid becomes supercooled. As the temperature of the supercooled liquid is lowered at some rate, a temperature is reached where the system falls out of equilibrium. At this temperature, often denoted as the glass transition temperature $T_g$, molecular motion becomes so slow that the molecules cannot rearrange on the time scale of the experiment. Kauzmann noted that if the entropy of the supercooled liquid is extrapolated to lower temperatures, it will equal the entropy of the crystal at a temperature not too far below $T_g$; the temperature where this occurs is referred to as the Kauzmann temperature $T_K$. While it is alarming enough that an amorphous state would have the same entropy as a well-ordered crystal, further entropy decreases along the extrapolated supercooled liquid line would result in a violation of the third law of thermodynamics. Thus it is generally accepted that the entropy of a supercooled liquid cannot continue to decrease along the extrapolated path as the temperature is lowered.

A number of resolutions to the entropy crisis have been proposed. Gibbs and DiMarzio proposed a second-order phase transition to an ideal glass at $T_K$, the glass transition temperature $T_g$, and the melting temperature $T_m$. Curve A (blue, dashed dot) illustrates the entropy of the supercooled liquid extrapolated to low temperature with a transition to an ideal glass at $T_K$. Curve B (red, dotted) shows a possible first-order phase transition, and curve C (green, dashed) illustrates a possible resolution without a phase transition.
between $T_g$ and $T_K$ (curve B). Experimental evidence for such a liquid—liquid transition has been reported for triphenyl phosphate, \textit{Al}$_2$O$_3$—Y$_2$O$_3$, and H$_2$O.\textsuperscript{16,17} Several models have also been proposed that support a liquid—liquid transition beginning with the free volume models of Cohen and Grest,\textsuperscript{18} along with the cooperative bond-lattice excitation models of Angell.\textsuperscript{19—21} A further alternate resolution to the entropy crisis is a continuous curve with no phase transition (curve C shows one possible example). Curves of this type were originally obtained from two-state models\textsuperscript{24,25} and recently have been observed in the exact numerical solutions to some model problems.\textsuperscript{26} Results similar to curve C have also been observed in a number of simulations rooted in work on the potential energy landscape.\textsuperscript{10,27,28} Understanding which of these resolutions (A, B, or C) is correct is important for predicting the mechanical and dynamical properties of amorphous materials above $T_g$. Theoretical treatments that attempt to describe dynamics above $T_g$ often begin with an idea or assumption about the thermodynamics of supercooled liquids below the conventional $T_g$.\textsuperscript{13,29—31}

In general, it has not been possible to experimentally determine how liquids resolve the entropy crisis. To do so requires access to the (metastable) equilibrium supercooled liquid at temperatures approaching $T_K$. While cooling a liquid more slowly maintains equilibrium to a lower temperature, molecular motions slow so precipitously as the temperature is lowered that thousands of years or more would be required to get even halfway to $T_K$ while maintaining equilibrium.

The potential energy landscape provides a useful language to describe the entropy crisis.\textsuperscript{10} The energy landscape controls the dynamics and thermodynamics of an amorphous N molecule system via the barrier heights and basin depths, respectively, of a surface with at least $3N + 1$ dimensions.\textsuperscript{32—34} At temperatures far above $T_g$, the system has sufficient energy to cross the barriers and sample configuration space. Below $T_g$, the system becomes stuck on the energy landscape; molecular rearrangements do allow for new configurations, but these can only be explored very slowly. Understanding the resolution of the entropy crisis requires access to the lower reaches of the energy landscape. For example, if curve A of Figure 1 is correct, the supercooled liquid would reach the bottom of the amorphous portion of the energy landscape at $T_K$.

We have recently shown that vapor deposition can be used to quickly prepare glasses that are low on the potential energy landscape.\textsuperscript{35,36} Highly stable glasses of 1,3,5-(tris)naphthylbenzene (TNB) and indomethacin (IMC) were formed from vapor deposition onto substrates with temperatures near 0.85 $T_g$. These glasses were up to 8 J/g lower in enthalpy and nearly 2% more dense than glasses prepared by cooling the liquid. The ability to create these glasses was attributed to enhanced mobility at the glass/vacuum interface where molecules can efficiently explore configuration space and thus find a lower position on the energy landscape. Until this recent work, the prevailing view in the literature was that vapor deposition results in high-enthalpy, low-density glasses.\textsuperscript{37—41} A recent paper by Kearns et al.\textsuperscript{36} shows that the substrate temperature is a key variable. Substrates held far below 0.85 $T_g$ result in less stable glasses, presumably because mobility at the surface is no longer fast enough to allow configurational sampling.

DSC Analysis. The details of the DSC analysis have been described elsewhere,\textsuperscript{46} and only the major points will be discussed here. A TA Instruments Q1000 DSC obtained three heating scans (10 K/min) for each sample. The first scan measured the heat capacity $C_p$ of the as-deposited glass. After this scan was complete, the sample was allowed to crystallize. The second scan determined the $C_p$ of the crystal allowing the
The black curve shows determined this to be the optimal temperature for preparing heating rates that produce these values. The properties of the substrate do not affect the observed $T$. Figure 2A shows the heat capacity curves observed for vapor-deposited IMC. The third scan measured the glass, and this sample is the basis of comparison with vapor-deposited glasses. The second scan, the sample was cooled at approximately 40 K/min. Inset: Structure of IMC. (B) Enthalpy curves obtained from integrating the $C_p$ curves in part A. The color of the lines shown in part A corresponds to the curves shown in part B. The temperature at which the extrapolated liquid line (black, dashed) intersects the enthalpy of the vapor-deposited glasses, and lower enthalpy glasses. We used Magill’s $C_p$ data for supercooled liquid enthalpy (dashed line). The IMC supercooled liquid $C_p$ is fit with Shamblin et al.’s data using

$$C_p(J/gK) = 3.10 \times 10^{-3} T/K + 6.8 \times 10^{-1}$$ (1)

The second-order polynomial that results to describe the enthalpy of the supercooled liquid is

$$H(J/g) = 1.55 \times 10^{-3} (T/K)^2 + 6.8 \times 10^{-1}T/K + C$$ (2)

Figure 3 is a summary of the $T_i$ values calculated for IMC vapor-deposited onto substrates held at 265 K. $T_i$ depends strongly on deposition rate. The lowest deposition rate results in a $T_i$ of 286 K, which is nearly 30 K below that of the ordinary glass. Similar data has been obtained for a second organic glass-former, TNB. Figure 4 shows both $C_p$ data (A) and the resulting enthalpy (B). $T_{\text{substrate}}$ for these depositions was 295 K ($\approx 0.85 T_g$) and the deposition rate was varied by a factor of 30. As for IMC, lower deposition rates produce larger enthalpy overshoots and lower enthalpy glasses. We used Magill’s $C_p$ data for supercooled TNB to extrapolate the supercooled liquid enthalpy to lower temperatures for the purpose of calculating $T_i$. The equation used for $C_p$ is

$$C_p(J/gK) = -6.31 \times 10^{-6} T/K^2 + 7.73 \times 10^{-3}T/K - 3.48 \times 10^{-1}$$ (3)
Integrating eq 3 gives the supercooled liquid enthalpy plotted in Figure 4B, which is

\[
H(\text{J/g}) = -2.103 \times 10^{-6}(T/\text{K})^3 + \\
3.865 \times 10^{-5}(T/\text{K})^2 - 3.48 \times 10^{-1}(T/\text{K}) + C
\]  

Figure 5. Summary of fictive temperatures \( T_f \) as a function of deposition rate for TNB. \( T_{\text{substrate}} \) was 295 K \((0.85 T_g)\) for each deposition. For the lowest deposition rate, the error bar indicates the range of \( T_f \) values obtained from two samples. For the two higher rates, the error bars indicate the uncertainty of the mass of sample, which was larger for these two samples.

\( T_f \) values for TNB calculated from Figure 4B are summarized in Figure 5. At the lowest deposition rate of 0.15 nm/s, the calculated \( T_f \) is 40 K below \( T_g \) of the ordinary glass. This \( T_f \) value is only 10 K higher than \( T_{\text{substrate}} \).

**Influence of Deposition Rate on Kinetic Stability.** Figure 6 shows the kinetic stability of vapor-deposited IMC and TNB glasses as a function of deposition rate. We use the onset temperature \( T_{\text{onset}} \) to quantify the kinetic stability. Below \( T_{\text{onset}} \) the sample is too immobile to absorb the heat needed to become a liquid. At \( T_{\text{onset}} \), the molecules begin to move, and an increase in heat capacity is observed as a consequence of configurational sampling. A higher \( T_{\text{onset}} \) signifies an increase in kinetic stability. Panel A of Figure 6 graphically defines \( T_{\text{onset}} \) as the intersection of the extrapolated glass line and the tangent drawn from the half-height of the enthalpy overshoot.

Panels B and C of Figure 6 show the deposition rate dependence of \( T_{\text{onset}} \) for IMC and TNB, respectively. For both materials, lowering the deposition rate increases \( T_{\text{onset}} \), indicating an enhancement of kinetic stability. \( T_{\text{onset}} \) values for the slowest deposition rates are at least 25 K greater than for the ordinary glass. By consideration of Figures 2–6 collectively, we note that lower depositions rates produce glasses with lower enthalpies and higher kinetic stabilities.

**Two Routes to Stability: Aging vs Deposition Rate.** One traditional way to produce low-energy glasses is to isothermally age a glass below \( T_g \). Glasses are in nonequilibrium states and relax slowly toward the more thermodynamically stable super-
the evolution of a glass toward the metastable supercooled liquid state through cooled liquid. Experimentally, one can characterize the progress of ordinary IMC glasses aged at 295 K for various periods of time. Comparison of aged and vapor-deposited IMC samples. (A) Figure 7A shows $C_p$ curves for both vapor-deposited and isothermally aged IMC samples. $T_{\text{substrate}}$ for the vapor-deposited sample was 295 K, and this is also the temperature at which the ordinary IMC glass was aged. The ordinary glasses shown in the figure were aged for up to 7 months. Each aging experiment was performed with approximately 5 mg of IMC in the same type of Al pan that was used for vapor deposition. The vapor-deposited samples were deposited at rates between 15 and 0.2 nm/s. As shown in Figure 7A, the ordinary glass aged for 7 months has similar kinetic stability to a glass vapor-deposited at 0.2 nm/s. These two samples also have the same enthalpy content and thus the same $T_i$ value (299 K). As the vapor-deposited sample described here was prepared in only 2 days, this high kinetic stability and low enthalpy content was achieved 100 times faster in the vapor-deposited sample than in the aged ordinary glass. Figure 7B contains a further comparison of aged and vapor-deposited glasses; it will be discussed below.

Figure 7A shows $C_p$ curves for multiple depositions of IMC at a $T_{\text{substrate}}$ of 265 K and a deposition rate of 0.5 nm/s. For the curves labeled IMC deposition 1 and 2, our intent was to produce two identical samples. While there are small differences in shape and $T_{\text{onset}}$ (perhaps due to slightly different deposition rates), both samples clearly show two peaks, indicating the reproducibility of this feature.

Double-Peaked $C_p$ Curves and the Influence of Water. As shown in Figure 2, deposition rates near 0.5 nm/s produce IMC glasses that show an interesting double-peaked enthalpy overshoot. Figure 8A presents $C_p$ curves for multiple depositions of IMC at a $T_{\text{substrate}}$ of 265 K and a deposition rate of 0.5 nm/s. The water-treated sample (blue) was subjected to humid ambient air (72% RH) for 12 h and 23 h of drying at 295 K before being analyzed. We observe that the water-treated IMC maintains a complicated enthalpy overshoot structure. A second peak is still observed, indicating the reproducibility of this feature.

We also studied the effect of humidity on the observed enthalpy overshoot since amorphous IMC is slightly hygroscopic. Figure 8A shows a sample that was subjected to humid ambient conditions and is designated as “water treated” in the figure. Initially, this IMC sample was vapor-deposited into a DSC pan using the same conditions that produced the other two samples shown in the figure. After this sample was removed from the vacuum chamber, it was treated with ambient humid air (72% RH) for 12 h. After this exposure the sample was placed back into the vacuum chamber for 23 h at room temperature to remove any absorbed water. Finally, the redried sample was removed from the chamber, and the DSC pan was sealed and placed in dry ice to prevent additional aging at room-temperature prior to DSC analysis.

Water exposure also has little impact on the enthalpy content as quantified by $T_i$; water exposure changed the calculated $T_i$ value by at most 2 K.

Discussion

We have shown that lowering the deposition rate increases the kinetic stability and lowers the enthalpy of vapor-deposited glasses of IMC and TNB. In this section, we rationalize our
results based on an enhanced surface mobility mechanism and describe the position of these samples on the potential energy landscape. We also discuss the origin of $C_p$ curves with multiple peaks and whether vapor deposition might be used to prepare equilibrium liquids below the glass transition temperature.

Enhanced Surface Mobility. There are many examples in the literature where enhanced surface mobility near $T_g$ has been observed or inferred in small-molecule and polymeric systems. Vapor deposition can utilize enhanced surface mobility to create a stable bulk glass. Mobile molecules at the glass/vacuum interface have the opportunity to explore configuration space and reach lower positions on the potential energy landscape. As the deposition progresses, the molecules that were at the interface are buried; these molecules now relax on the much slower time scale of the bulk glass. In the meantime, new molecules arrive and rapidly sample configurations at the surface, and the process continues. Eventually this layer-by-layer process produces a bulk glass in which the molecules are locked into low-energy configurations.

The deposition rate dependence of the enthalpy and kinetic stability strongly supports this enhanced surface dynamics mechanism. Molecules that are in the mobile surface layer sample configurations until being trapped in the bulk. Lower deposition rates give the surface molecules more time for configuration sampling. Thus glasses with low enthalpies can be created as shown in Figures 2–5. These more stable local packing arrangements naturally give rise to higher onset temperatures for mobility as shown in Figure 6. Of course, this is only possible if $T_{\text{substrate}}$ is such that substantial surface mobility exists, as discussed previously.

We can use the dependence of the enthalpy on the deposition rate to compare the dynamics at the surface to those in the bulk as illustrated in Figure 7B. Fictive temperatures are plotted as a function of the relevant equilibration time for vapor-deposited samples and for ordinary glasses aged for different time periods. For the aged samples, $T_f$ is plotted against the total annealing time at 295 K (up to 210 days). For the vapor-deposited samples, we plot $T_f$ against the surface equilibration time $t_{\text{surface}}$ since all the relevant configuration sampling occurs while the molecules are near the surface. Any bulk relaxation that may have taken place during the deposition is negligible. For this calculation, we assume that the mobile surface layer is 1 nm thick and calculate $t_{\text{surface}} = (1 \text{ nm})/(\text{deposition rate})$. The horizontal dotted line in the graph represents the expected $T_f$ for both samples once thermodynamic equilibrium has been reached.

Figure 7B shows that mobility at the surface of IMC glasses at 295 K is about $10^7$ times faster than bulk mobility since the two solid lines are displaced by this factor. The intersection of the solid lines with the dotted line is a rough estimate of the two solid lines are displaced by this factor. The intersection of the relevant equilibration time for vapor-deposited glasses and for ordinary glasses aged for different time periods.

Hiking down the Energy Landscape. As discussed in the introduction, glasses prepared by cooling the liquid get stuck on the potential energy landscape at $T_g$. Further progress down the landscape is very slow because of the extremely long time required for molecular rearrangements in a bulk glass. If we accept that an amorphous system will not have an entropy significantly lower than the crystal, then the resolution to the entropy crisis lies near the bottom of the amorphous part of the potential energy landscape, somewhere below the portion of the landscape readily accessed by traditional glasses. Vapor-deposited glasses, due to rapid configurational sampling at the glass/vacuum interface, partially circumvent this kinetic limitation.

There is a direct, quantitative relationship between the enthalpy of a glass (as determined in our experiments) and its average position on the potential energy landscape. It can be shown that

$$\epsilon(\text{stable glass}) - \epsilon(\text{ordinary glass}) \approx H(\text{stable glass}) - H(\text{ordinary glass}) \quad (5)$$

where $\epsilon$ represents the average energy of the minima of occupied potential energy basins. Thus, a vapor-deposited glass whose enthalpy content is 10 J/g lower than an ordinary glass is also approximately 10 J/g lower on the potential energy landscape. Two approximations are made in deriving eq 5. First, the enthalpy is equated with the internal energy; this approximation is good to better than 0.01 J/g. Second, the internal energy is approximated as a sum of configurational and vibrational contributions, and the vibrational contributions of the two glasses are equated. Accurate comparisons of $C_p$ for stable and ordinary glasses can determine the accuracy of this approximation; the error in eq 5 is likely to be less than 1 J/g.

We have defined a quantity $\theta_K$ that describes the position of a glass on the potential energy landscape relative to an ordinary glass that leaves equilibrium upon cooling at $T_g$.

$$\theta_K = \frac{T_g - T_f}{T_g - T_K} \quad (6)$$

When $\theta_K$ is equal to zero, a vapor-deposited sample has not progressed any further down the landscape than can be achieved by cooling the supercooled liquid at a rate on the order of 10 K/min; $T_f$ is equal to $T_g$. On the other hand, a value of one indicates that a vapor-deposited glass has reached the bottom of the amorphous portion of the potential energy landscape. Equation 6 assumes that the entropy of the supercooled liquid follows curve A in Figure 1 and that the entropy of an amorphous state cannot be lower than the entropy of the crystal.

Figure 9 shows $\theta_K$ values for IMC and TNB glasses prepared by vapor deposition and by aging the ordinary glass for various periods of time. $\theta_K$ values for vapor-deposited IMC and TNB glasses deposited at the lowest rates are 0.39 and 0.42, respectively. These samples have progressed about 40% of the way toward the bottom of the amorphous portion of the energy landscape relative to an ordinary glass. Aging ordinary glasses of TNB or IMC below $T_g$ for weeks to months produces glasses that are at most 24% of the way to the bottom of the landscape.
Figure 9. $\theta_K$ values for vapor-deposited and aged glasses. As explained in the text, larger $\theta_K$ values indicate glasses with lower positions on the potential energy landscape. The values indicated for the vapor-deposited IMC and TNB samples are for samples deposited at rates of 0.2 and 0.15 nm/s, respectively. The aged IMC sample was held at 295 K for 210 days. TNB was aged at 295 K for 320 days and at 328 K for 15 days. The PVAc $\theta_K$ value was determined from experiments performed by Kovacs55 in which PVAc was annealed at 298 K for 2 months. Although vapor-deposited samples are prepared much more quickly than the aged samples, they are significantly lower on the energy landscape.

Also shown in Figure 9 is $\theta_K$ data for Kovacs’ seminal aging experiments on PVAc.55 Aging PVAc for 2 months results in a $\theta_K$ value of 0.17 or less, depending on the $T_N$ value used.55,56

To provide some perspective on the $\theta_K$ values achieved by these vapor-deposited glasses, we estimate the time required to age an ordinary glass to these $\theta_K$ values. We do this calculation for TNB with $\theta_K = 0.42$ (as shown in Figure 9). Consistent with aging experiments near $T_N$, we assume that the time required to age an ordinary glass to equilibrium is roughly equal to the equilibrium structural relaxation time ($\tau_\alpha$) at the aging temperature. The vapor-deposited sample has $T_\alpha = 307$ K, and we estimate $\tau_\alpha$ at 307 K using $\tau_\alpha = 140$ s at 344 K (based on the dielectric relaxation measurements of Richert et al.58) and the extrapolated temperature dependence of $\tau_\alpha$. Our estimate for $\tau_\alpha$ at 307 K is $10^{19}$ s, $10^{12}$ s, or $10^9$ s, depending upon whether we use a non-Arrhenius extrapolation of the temperature dependence of the dielectric58 and viscosity57 data, or an Arrhenius extrapolation of the viscosity data, respectively. Thus we estimate that the time required to age an ordinary glass of TNB to the same position on the energy landscape as we have obtained by vapor deposition to be somewhere between one thousand years and one trillion years. There is no way of knowing which of these extrapolations is most realistic. In any case, as our vapor-deposited samples required less than a few days to prepare, it is clear that vapor deposition provides a route to the lower reaches of the energy landscape that is at least 10^5 times more efficient than cooling a liquid.

An unsatisfying feature of $\theta_K$ (eq 6) is that its construction assumes a particular resolution to the entropy crisis. While we can unambiguously establish the position of vapor-deposited samples on the energy landscape relative to ordinary glasses using eq 5, establishing the position relative to the bottom of the amorphous portion of the landscape necessarily involves assumptions; different resolutions to the entropy crisis will place the bottom of the amorphous portion of the landscape at different levels. An alternate method of characterizing our vapor-deposited samples uses the enthalpy of the crystal as the reference point; the crystalline state is regarded as the bottom of the energy landscape. For TNB, the ordinary glass has an enthalpy that is 58 J/g above the crystal enthalpy. The enthalpy of our most stable vapor-deposited TNB glass is 45 J/g above the crystal enthalpy. Thus this vapor-deposited sample is 22% of the way to the absolute bottom of the landscape relative to an ordinary glass.

Finally, we make a technical comment about calculations involving eq 6. For IMC and TNB, we used $T_K$ values taken from the literature (240 K for IMC, 46 250 K for TNB). These values are within a few kelvin of the $T_K$ values calculated from eqs 1 and 3 and the known temperature dependence of $C_p$ for the crystals, based on the assignment of $T_G$ as the temperature where the excess entropy is zero.46 Some authors define $T_K$ as the temperature where the configurational entropy goes to zero. $T_K$ would then be 250 K for IMC and 270 K for TNB resulting in $\theta_K$ values of 0.45 and 0.53 for IMC and TNB, respectively.

Can Vapor Deposition Create a Low-Temperature Supercooled Liquid? To study the Kauzmann entropy crisis directly, one must create low-temperature equilibrium supercooled liquids and measure their entropy. The crisis, as usually stated, pertains to (metastable) equilibrium supercooled liquids and not nonequilibrium glass systems.5 If equilibrium supercooled liquids can be obtained by vapor deposition, we assume that one must deposit at rates low enough that further decreasing the deposition rate does not change the properties of the sample. Under these conditions, we imagine that the molecules at the top surface of the deposited film have enough time to explore configuration space and find the equilibrium distribution of local arrangements for the temperature of the substrate. Our current range of deposition rates is limited by the 2–4 mg of sample needed for analysis with conventional DSC. Since $T_\tau$ and $T_{\text{onset}}$ are still changing with deposition rate, we assume that we have not yet reached the equilibrium supercooled liquid. We are exploring other analysis techniques that will allow us to lower the deposition rate at least another 2 orders of magnitude.

It may be that deposition into an equilibrium bulk supercooled liquid will not be possible for a given material. Figure 7A shows data for IMC samples that were either vapor-deposited with $T_{\text{substrate}}$ equal to 295 K or aged at room temperature ($\approx$295 K). These samples have similar $T_\tau$ values, and yet their $C_p$ curves have dissimilar shapes, indicating that these two glasses are not the same. This may indicate that the equilibrium local packing of molecules at the surface may differ from that in the bulk. Alternatively, the dissimilar shapes could signify that there is a much broader distribution of relaxation times for the vapor-deposited sample. Nonetheless, neither sample has yet reached thermodynamic equilibrium. Upon further aging and slower deposition, $C_p$ curves for aged and vapor-deposited samples may overlap each other meaning vapor-deposition can produce equilibrium bulk supercooled liquids.

We have made efforts to vapor-deposit IMC glasses at even lower deposition rates. Preliminary results indicate that the trend for $T_{\text{onset}}$ shown in Figure 6B continues, while the trend for $T_\tau$ shown in Figure 3 does not. A single deposition of IMC at a rate of 0.08 nm/s with a $T_{\text{substrate}}$ of 265 K was attempted. The $T_\tau$ calculated for this sample was approximately 10 degrees higher than that deposited at 0.2 nm/s, while a sharpening of the enthalpy relaxation peak was also observed. Clearly this behavior needs to be carefully explored for a number of different materials in order to understand under what circumstances vapor deposition can prepare equilibrium supercooled liquids. Unfortunately, the mass limitations of conventional DSC make it
unsuitable for these low deposition rates. As mentioned above, new techniques are being explored to circumvent this limitation.

**Origin of C_p Curves with Multiple Peaks.** Figures 2 and 4 show that vapor deposition of both IMC and TNB can result in glasses that have C_p curves with complex shapes. In particular, IMC with T_{substrate} at 265 K and a rate of 0.5 nm/s results in a double-peaked structure as shown in Figures 2 and 8. We believe that these two peaks are an indication of two different types of local packing in the vapor-deposited glass. In this scenario, the peak at higher temperature corresponds to a more stable structure that does not “melt” into the liquid until a higher temperature. We are currently exploring other techniques to determine if indeed two different local packings are present in the sample.

In terms of the potential energy landscape, C_p curves with peaks could perhaps indicate that we are approaching the bottom of the landscape. At low positions in the landscape, the system can only sample low-energy configurations. For low enough energies there may be only a few possible local packings. If only two types of local packing were possible, this would explain an enthalpy overshoot with two distinct peaks.

**Conclusions**

Physical vapor deposition was used to prepare glasses of two organic molecules: IMC and TNB. The substrate temperature was held at 0.85 T_f for most experiments, and the deposition rates varied from 13 to 0.15 nm/s. The enthalpy and kinetic stability for each glass was quantified by determining the fictive temperature T_f and the mobility onset temperature T_onset. The slowest deposition rates resulted in the lowest enthalpies and the greatest kinetic stabilities. Vapor deposition can create low-energy glasses much more rapidly than aging. For TNB depositions at 0.85 T_f, we have progressed more than 40% of the way to the bottom of the amorphous portion of the potential energy landscape with samples that required only a few days to prepare. We estimate that aging an ordinary glass to a similar position on the landscape would require between one thousand and one trillion years, depending upon assumptions about structural relaxation in low-temperature supercooled liquids.

We attribute the ability to create these stable vapor-deposited glasses to a surface layer with enhanced mobility. We estimate that the dynamics at the glass/vacuum interface of IMC are about 7 orders of magnitude faster than bulk dynamics at 295 K. The dynamics at the glass/vacuum interface of IMC are about 10 orders of magnitude faster than bulk dynamics at 295 K. The mobility onset temperature T_onset is important. Changes to the absorption producing amorphous materials that are stable against environmental perturbations is important. Changes to the absorption spectrum of amorphous Alq3 films, a system often used in OLEDs, have been observed after exposure to ambient atmospheric conditions.50,60 Andronis et al.48,49 showed that crystallization rates in amorphous IMC greatly increased when water vapor was present in the sample. We are currently studying water uptake in IMC glasses to determine the extent to which vapor-deposited glasses might better resist environmental changes.

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**References and Notes**