Vapor-Deposited Ethylbenzene Glasses Approach "Ideal Glass" Density

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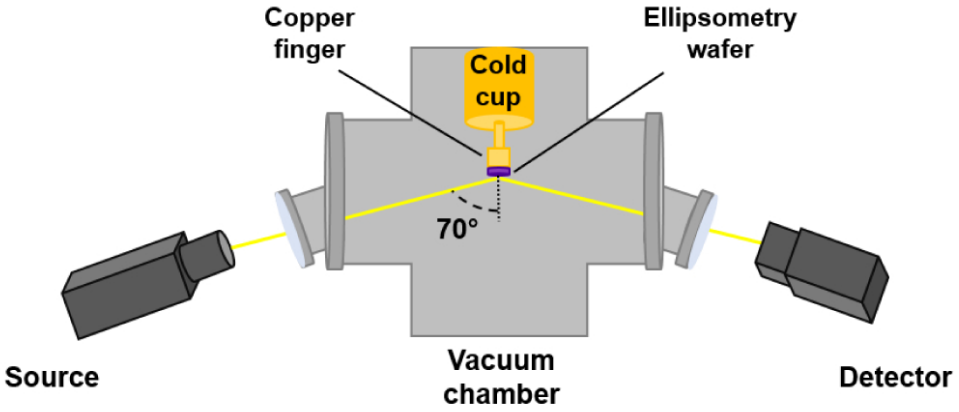

Figure 1. Schematic of in situ ellipsometry experiment. The source and detector are both fixed at a 70° angle relative to the surface normal of the silicon substrate.

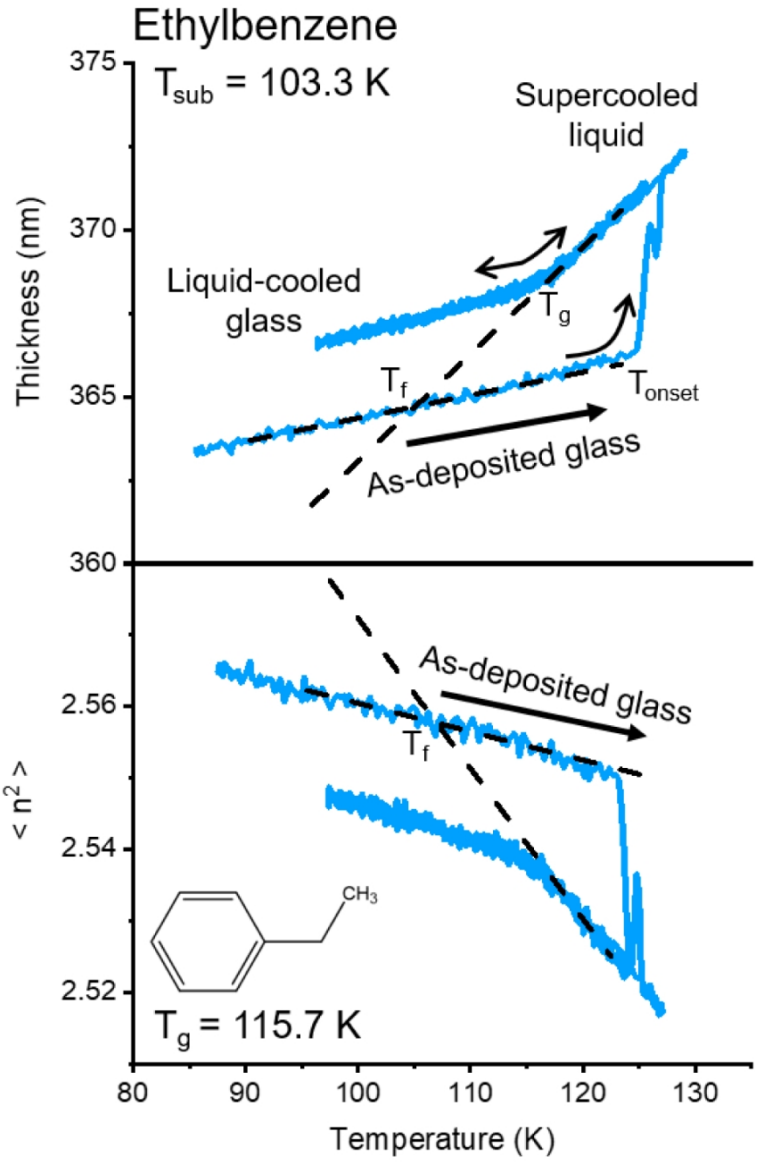

Figure 2. In situ ellipsometry data from ramping experiments of ethylbenzene deposited at Tsub = 103.3 K (0.89 Tg) with a rate of 0.7 nm/s illustrating the increased density and kinetic stability of the PVD glass. The top panel shows the thickness of the as-deposited glass in comparison with the liquid-cooled glass. The bottom panel shows mean-squared refractive index (<n2>). The black dashed lines are fits to the data for the glasses and supercooled liquid. The intersection of the extrapolated supercooled liquid line and as-deposited glass fit defines the fictive temperature, Tf. The intersection of the supercooled liquid and liquid-cooled glass fits define Tg. The structure of ethylbenzene is shown in the bottom panel.

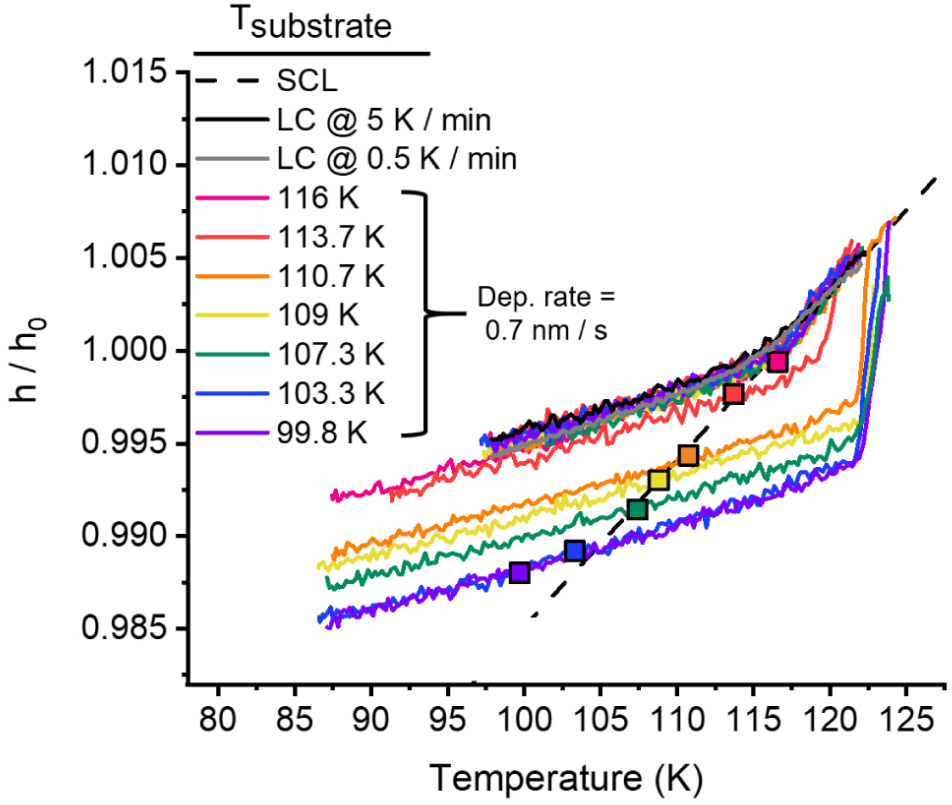

Figure 3. Normalized change in thickness as a function of temperature for glasses of ethylbenzene deposited at 0.7 nm/s. The colored curves represent PVD glasses prepared at the indicated substrate temperatures. The heating curve for the as-deposited glass and the first heating curve for the corresponding liquid-cooled glass are shown. The black and grey curves show results for liquid-cooled glasses cooled at 5 K/min and 0.5 K/min, respectively. The black dashed line is the extrapolation of the equilibrium supercooled liquid. Colored squares represent the normalized change in thickness at the deposition temperature. When these squares lie on the dashed line, the densities measured are consistent with the density expected for the supercooled liquid. For clarity, only the glasses prepared with a deposition rate of 0.7 nm/s are shown.

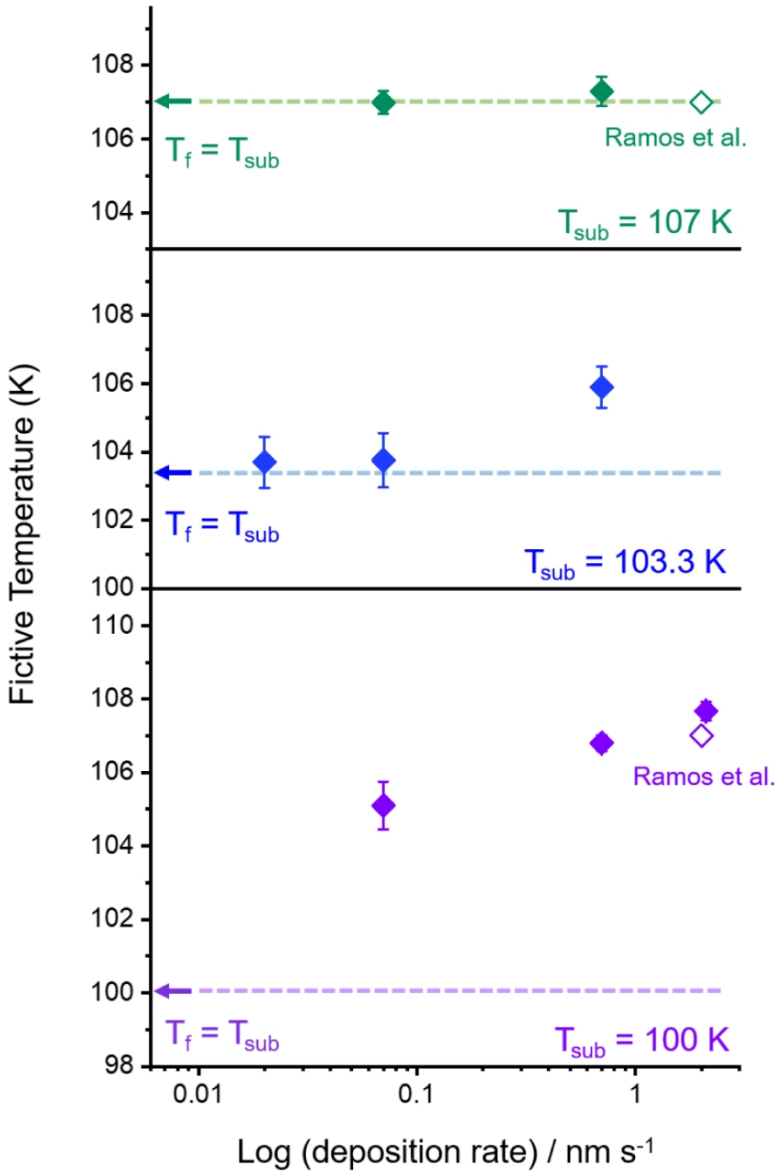

Figure 4. Fictive temperatures as a function of deposition rate for glasses deposited at 107 K (green, top), 103.3 K (blue, middle) and 100 K (purple, bottom). The solid points are fictive temperatures calculated from density measurements. Arrows and dashed lines indicate where Tf = Tsub. The open points represent enthalpy measurements by Ramos et al.32

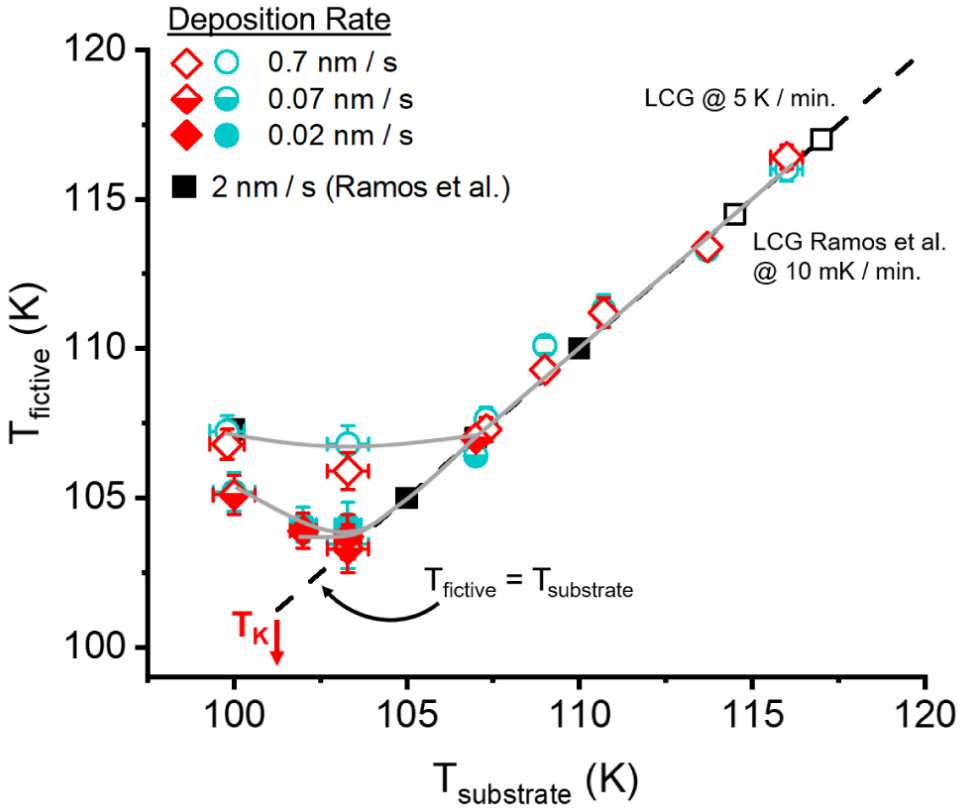

Figure 5. Fictive temperature as a function of substrate temperature during deposition for ethylbenzene glasses prepared at several rates. At low deposition rates, PVD glasses have the properties expected for the supercooled liquid to within 2 K of TK. Red symbols are calculated from thickness measurements, teal symbols are calculated from refractive index measurements, and black squares from enthalpy measurements.32 Open squares represent liquid-cooled glasses with cooling rates indicated. The arrow indicates the location of TK as reported by Ref. 7. The grey solid lines are guides to the eye illustrating trends for different deposition rates.

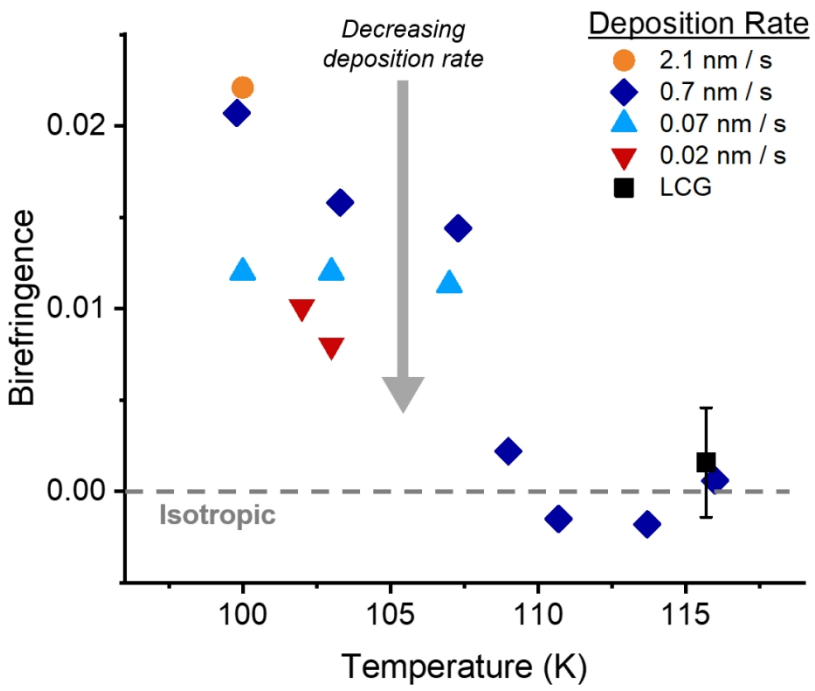

Figure 6. Birefringence as a function of substrate temperature for vapor-deposited glasses of ethylbenzene, with deposition rates indicated in the legend. The black open square is the average birefringence of all glasses prepared by cooling the liquid at 5 K/min; the error bar indicates one standard deviation. Error bars for the PVD glasses are expected to be comparable.

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Vapor-Deposited Ethylbenzene Glasses Approach "Ideal Glass" Density

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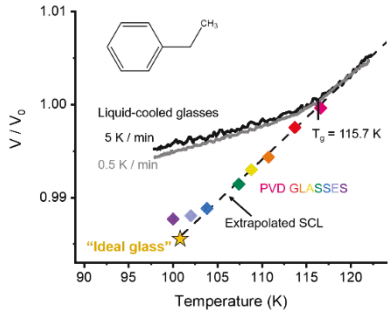
TOC Figure:



Abstract: Spectroscopic ellipsometry was used to characterize vapor-deposited glasses of ethylbenzene (T_g = 115.7 K). For this system, previous calorimetric experiments have established that a transition to the ideal glass state is expected to occur near 101 K (the Kauzmann temperature, T_K) if the low temperature supercooled liquid has the properties expected based upon extrapolation from above T_g. Ethylbenzene glasses were vapor-deposited at substrate temperatures between 100 K (~0.86 T_g) and 116 K (~T_g), using deposition rates of 0.02 – 2.1 nm/s. Down to 103 K, glasses prepared in the limit of low deposition rate have densities consistent with the extrapolated supercooled liquid. The highest density glass is within 0.15% of the density expected for the ideal glass. These results support the hypothesis that the extrapolated properties of supercooled ethylbenzene are correct to within just a few Kelvin of T_K, consistent with the existence of a phase transition to an ideal glass state at T_K.

Glasses are non-equilibrium materials and thus their properties depend upon how they are prepared. For example, for a typical liquid with a positive thermal expansion coefficient, the glass prepared by cooling at 1 K/min will be denser than the glass prepared by cooling at 10 K/min. Slower cooling allows the liquid to remain in equilibrium down to lower temperatures where the density is higher. This scenario might suggest that the liquid density would continue to rise if the liquid could be equilibrated even as temperature approached T = 0 K, but there are good reasons to think that this is not the case. Kauzmann described how the entropy provides a bound on the properties of the amorphous state.[1] The entropy of a supercooled liquid typically decreases more rapidly with temperature than does the crystal entropy. If this trend continued unabated down to T=0 K, the entropy of the liquid would be less than the entropy of the crystal, in violation of the 3rd law of thermodynamics.[2] For understanding glass formation, it is useful to consider the configurational part of the liquid entropy as this quantity decreases rapidly with decreasing temperature and must remain positive. In the limit in which a liquid is cooled infinitely slowly, a number of scenarios have been suggested to avoid the configurational entropy crisis, including a phase transition to an "ideal glass" state at a temperature denoted the Kauzmann temperature (T_K).[3-4] Conventionally, T_K is defined as the temperature where the extrapolated configurational entropy is zero. In this scenario, the ideal glass is the amorphous state with the lowest position on the potential energy landscape.

One current theoretical approach supports the idea of a phase transition at T_K, positing a random first order transition to the ideal glass.[5] Some recent computer simulations support this scenario, showing a precipitous decrease of the liquid entropy as temperature is decreased and direct indications of an increasing structural length scale associated with this loss of entropy.[6-7] While many experiments[8] are consistent with a transition to an ideal glass at T_K, this is clearly not

the only possible resolution to the entropy crisis.[2] Alternatively, a first-order phase transition could occur between T_g and T_K; evidence for liquid-liquid transitions has been reported triphenyl phosphite[9-10], Al_2O_3-Y_2O_3[11], and water.[12-15] The free volume models of Cohen and Grest[16] and the cooperative bond-lattice excitation models of Angell[17-18] also suggest a first-order phase transition as the resolution to the entropy crisis. Another possibility, a continuous change in liquid properties, without a phase transition, has also been suggested;[19] behavior of this type has been obtained from two-state models[20] and computer simulations of specific systems.[21-24]

While it is important to understand the resolution to the Kauzmann entropy crisis, it is difficult to do so because the liquid must remain in equilibrium as T_K is approached. Liquids cooled from above the melting temperature get "stuck" on the energy landscape well above T_K; as the system is cooled at a fixed rate, it falls out of equilibrium when the time required for molecular motion exceeds that available.[25-26] Since molecular motions slow down dramatically as temperature is lowered, cooling times well beyond experimental timescales would be required to attain equilibrium even halfway from T_g to T_K. This limitation naturally leaves the question "do supercooled liquids below the glass transition temperature have the properties expected by extrapolation?" unanswered. In order to understand how the entropy crisis might be resolved, non-traditional preparation techniques must be utilized to access states lower in the potential energy landscape. Experiments on geologically aged glasses[27] and swap Monte Carlo computer simulations are possible routes for approaching the ideal glass state.[6-7] The swap Monte Carlo simulations have been used to prepare equilibrium supercooled liquids down to much lower temperatures than previously possible,[6-7] and are consistent with a phase transition to an ideal glass state at T_K.[28-30]

Physical vapor deposition (PVD) is a promising route for the preparation of glasses low on the potential energy landscape.[31-34] PVD glasses have properties expected for glasses cooled at extremely low rates since rapid surface equilibration during deposition allows the kinetic restrictions of bulk cooling to be circumvented. In 2011, Ramos et al. published high precision adiabatic calorimetry measurements on PVD glasses of ethylbenzene ($T_g \approx 116$ K).[33] They found that glasses deposited at substrate temperatures from 105 to 110 K had the enthalpies expected for the extrapolated supercooled liquid at the given substrate temperatures and are thus very low in the potential energy landscape. One interpretation of these results is that, at the deposition rate used (2 nm/s), glasses vapor-deposited with substrate temperatures down to 105 K (T_K + 4 K) are accurate models for the equilibrium supercooled liquid. Still, this calorimetry work left significant questions unanswered: Are the properties of these PVD glasses independent of deposition rate, as would be expected if equilibrium had been attained? Are PVD glasses of ethylbenzene structurally isotropic, as expected for the equilibrium supercooled liquid? Can glasses with properties consistent with the extrapolated supercooled liquid be obtained even closer to T_K?

In order to answer these questions, we investigate how the densities of PVD glasses of ethylbenzene depend on a wide range of substrate temperatures and deposition rates. In addition to the work of Ramos et al.[33], ethylbenzene has been well-characterized by dielectric spectroscopy[35], adiabatic calorimetry[25], nanocalorimetry[34, 36-38] light scattering experiments[39-40], and atomistic simulations.[41] We find that glasses of ethylbenzene deposited at temperatures between 107 K and 116 K have densities consistent with the extrapolated supercooled liquid when prepared with deposition rates near 0.7 nm/s. In this temperature range, the enthalpy of PVD glasses of ethylbenzene is also consistent with high temperature extrapolations.[33] If slower deposition rates are used, either 0.07 nm/s or 0.02 nm/s, we can prepare ethylbenzene glasses at a

substrate temperature of 103 K that also have the density expected for the extrapolated supercooled liquid. Based on these results, we expect that PVD glasses can serve as accurate models for the equilibrium supercooled liquid. Our results support the hypothesis that the extrapolated properties of supercooled ethylbenzene are correct to within just a few Kelvin of T_K, consistent with the existence of a phase transition to an ideal glass state at T_K.

In situ spectroscopic ellipsometry was used to characterize PVD glasses of ethylbenzene as schematically illustrated in Figure 1. Glass films roughly 400 nm thick were deposited onto a temperature-controlled silicon wafer. The ellipsometer source and detector were attached to the vacuum chamber and both fixed at a 70° angle relative to the surface normal of the silicon wafer. The ellipsometric data were fit in the 350 – 1000 nm wavelength range to an anisotropic Cauchy model. Further modelling details are provided in the Methods section.

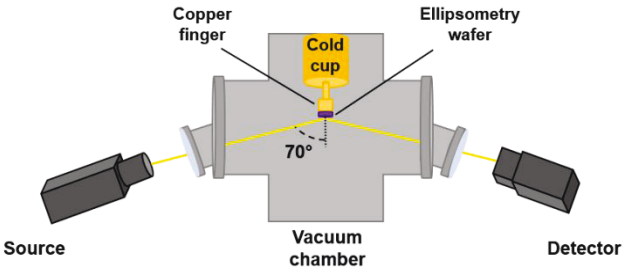


Figure 1. Schematic of in situ ellipsometry experiment. The source and detector are both fixed at a 70° angle relative to the surface normal of the silicon substrate.

Figure 2 illustrates the increased density and thermal stability of PVD ethylbenzene glasses, showing data obtained while increasing temperature at 5 K/min. The ethylbenzene glass shown in Figure 2 was deposited at T_{sub} = 103.3 K. Following deposition, the glass was first cooled to 90 K, heated to above the T_g and then cooled to prepare a liquid-cooled glass. The liquid-cooled

glass was then heated and cooled two additional times. All heating and cooling was performed at 5 K/min. As expected based on previous results[42], the PVD glass is thinner and thus denser than the liquid-cooled glass. Additionally, the PVD glass has a higher refractive index. Since ethylbenzene glasses can be anisotropic (birefringence is discussed below) we report the mean-squared refractive index,[42-43] $< n^2 >$, as follows:

$$< n^2 > = \frac{{n_e}^2 + 2{n_o}^2}{3} \quad (1)$$

Here, n_e is the refractive index out of the plane of the substrate and n_o is the refractive index in the plane of the substrate. Figure 2 also illustrates the definition of the fictive temperature (T_f). We extrapolate the fitted line of the supercooled liquid to intersect the as-deposited glass curve; the intersection point is T_f. Each experiment yields two fictive temperatures, characterizing the density and refractive index of the vapor-deposited glass; $T_f = T_{sub}$ means that the as-deposited glass has the density or refractive index expected for the (extrapolated) supercooled liquid.

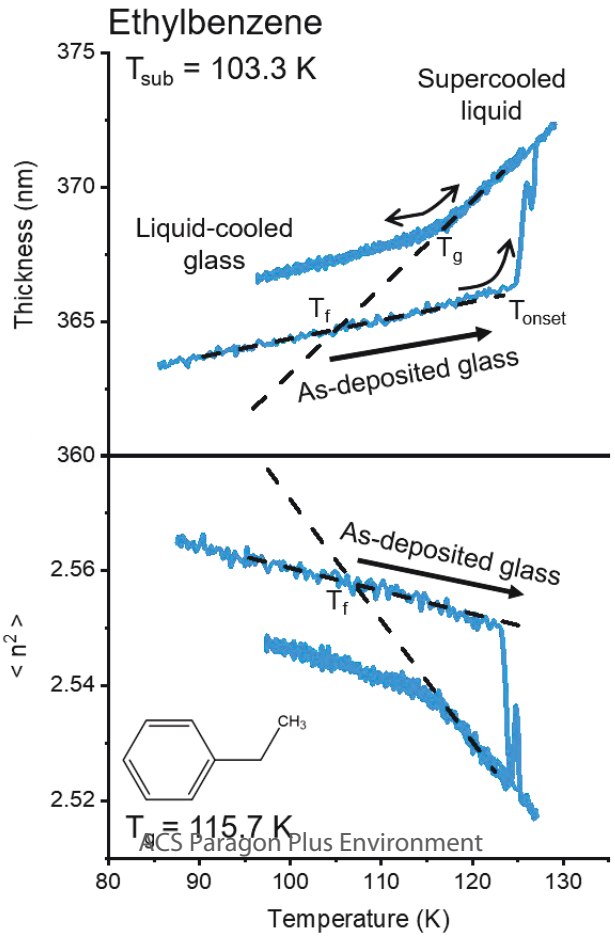


Figure 2. In situ ellipsometry data from ramping experiments of ethylbenzene deposited at T_{sub} = 103.3 K (0.89 T_g) with a rate of 0.7 nm/s illustrating the increased density and kinetic stability of the PVD glass. The top panel shows the thickness of the as-deposited glass in comparison with the liquid-cooled glass. The bottom panel shows mean-squared refractive index ($<n^2>$). The black dashed lines are fits to the data for the glasses and supercooled liquid. The intersection of the extrapolated supercooled liquid line and as-deposited glass fit defines the fictive temperature, T_f. The intersection of the supercooled liquid and liquid-cooled glass fits define T_g. The structure of ethylbenzene is shown in the bottom panel.

Figure 3 compares all glasses of ethylbenzene deposited at 0.7 nm/s over a range of substrate temperatures and illustrates that PVD glasses prepared with substrate temperatures as low as 107 K have densities consistent with the supercooled liquid. The colored curves show the normalized thickness change of the as-deposited glasses upon initial heating and the subsequent heating scan for the corresponding liquid-cooled glass. The change in thickness is inversely proportional to the change in density. The black and grey curves show data for liquid-cooled glasses prepared at two cooling rates, 5 K/min and 0.5 K/min, respectively. The solid points show the normalized change in thickness at each substrate temperature. The black dashed line is the extrapolation of the equilibrium supercooled liquid. Down to substrate temperatures of 107.3 K, the PVD glasses prepared with a deposition rate of 0.7 nm/s have densities consistent with those

expected for the supercooled liquid. This substrate temperature range also results in PVD glasses with enthalpies that are consistent with high temperature extrapolations.[33] For substrate temperatures below 107.3 K, deposition at 0.7 nm/s does not produce glasses that have densities consistent with those expected for the supercooled liquid (as illustrated by the colored squares that do not lie on the line).

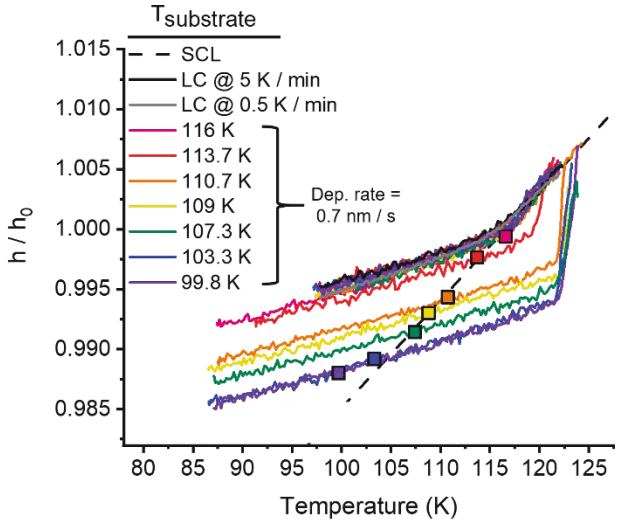


Figure 3. Normalized change in thickness as a function of temperature for glasses of ethylbenzene deposited at 0.7 nm/s. The colored curves represent PVD glasses prepared at the indicated substrate temperatures. The heating curve for the as-deposited glass and the first heating curve for the corresponding liquid-cooled glass are shown. The black and grey curves show results for liquid-cooled glasses cooled at 5 K/min and 0.5 K/min, respectively. The black dashed line is the extrapolation of the equilibrium supercooled liquid. Colored squares represent the normalized change in thickness at the deposition temperature. When these squares lie on the dashed line, the densities measured are consistent with the density expected for the supercooled liquid. For clarity, only the glasses prepared with a deposition rate of 0.7 nm/s are shown.

Figure 4 illustrates how lower deposition rates can be used to increase the range of substrate temperatures for which the extrapolated supercooled liquid density is attained. For glasses deposited at 107 K (green, top panel), films prepared at two different rates have fictive temperatures equal to the substrate temperature; we interpret this to mean that both rates are slow enough to achieve the equilibrium density during deposition. For glasses deposited at 103.3 K (blue, middle panel), lowering the deposition rate from 0.7 nm/s produces denser glasses as indicated by the lower fictive temperatures. The good agreement between fictive temperatures for the two slower depositions suggests that the equilibrium density is attained already with the intermediate deposition rate. For the lowest substrate temperature shown, 100 K (purple, bottom panel), lowering the deposition rate smoothly increases the density. We conclude that even lower deposition rates would be required to reach the equilibrium density. The fictive temperatures in Figure 4 are in excellent agreement with those obtained from the enthalpy measurements of Ramos et al.[33] In comparison with reference [33], lower deposition rates could be achieved with the ellipsometry measurements since much thinner films can be utilized, allowing us to extend the temperature range where PVD glass properties match those of the extrapolated supercooled liquid.

Based on the extrapolation of Tatsumi et al.[8], equilibration at 103.3 K instead of 105 K lowers the configurational entropy by 30%.

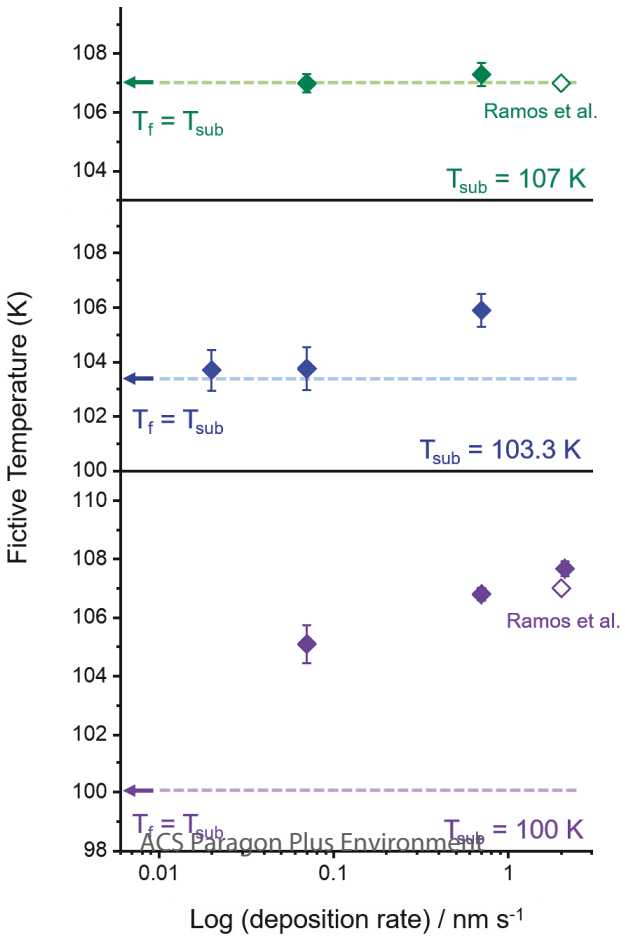


Figure 4. Fictive temperatures as a function of deposition rate for ethylbenzene glasses deposited at 107 K (green, top), 103.3 K (blue, middle) and 100 K (purple, bottom). The solid points are fictive temperatures calculated from density measurements. Arrows and dashed lines indicate where $T_f = T_{sub}$. The open points represent enthalpy measurements by Ramos et al.[33]

By utilizing lower deposition rates, ethylbenzene glasses can be prepared that have properties consistent with the extrapolated supercooled liquid down to a temperature only a few Kelvin above T_K. Figure 5 illustrates the fictive temperatures of glasses prepared with a range of substrate temperatures and deposition rates. The black dashed line shows $T_f = T_{sub}$; the points that fall on this line represent glasses that have properties consistent with those expected for the supercooled liquid. Three different properties are compared in Figure 5. The colored points show fictive temperatures for the density and refractive index for the ethylbenzene glasses prepared in this work. The black squares represent the enthalpy measurements of Ramos et al.[33] for glasses deposited at 2 nm/s. There is excellent agreement between the fictive temperatures calculated from these three observables. In other words, in the limit of low deposition rates, the density, enthalpy, and refractive index of vapor-deposited glasses are all consistent with the values expected for the

supercooled liquid. Figure 5 establishes that PVD glasses of ethylbenzene can approach the limit of "ideal glass" packing. The glasses deposited at 0.02 nm/s at T_{sub} = 103.3 K are only 0.15% less dense than the ideal glass (based upon extrapolation to 101 K).

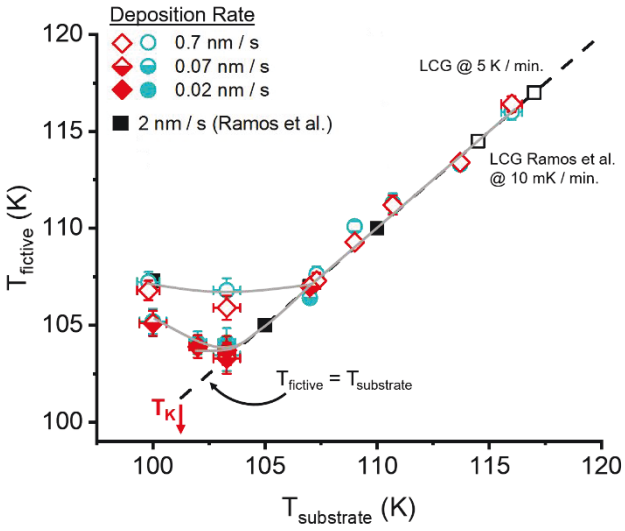


Figure 5. Fictive temperature as a function of substrate temperature during deposition for ethylbenzene glasses prepared at several rates. At low deposition rates, PVD glasses have the properties expected for the supercooled liquid to within 2 K of T_K. Red symbols are calculated from thickness measurements, teal symbols are calculated from refractive index measurements, and black squares from enthalpy measurements.[33] Open squares represent liquid-cooled glasses with cooling rates indicated. The arrow indicates the location of T_K as reported by Ref. [8]. The grey solid lines are guides to the eye illustrating trends for different deposition rates.

While Figure 5 illustrates the progress gained toward the Kauzmann temperature by depositing glasses more slowly, it is worth noting that there is potential uncertainty in the value of T_K. Based upon adiabatic calorimetry data on the crystal, supercooled liquid, and liquid-cooled glass of ethylbenzene, Yamamuro et al. reported a Kauzmann temperature of 101 K.[8] Their calculation of the configurational entropy of the supercooled liquid includes a term that corrects

for the difference in vibrational entropy between the glass and crystal. However, recent work[36] has shown that PVD glasses of ethylbenzene deposited near 103 K have heat capacities in the temperature range just below T_g that are roughly 2.5% lower than a liquid-cooled glass. If we accept that the highest density vapor-deposited glass is a better model for the ideal glass than is the liquid-cooled glass, the value of T_K will shift. To estimate the magnitude of this correction, we apply the 2.5% decrease in heat capacity in the temperature window from 90 K to 116 K. Previous work has shown a correlation between the diminished heat capacity and suppression of secondary relaxations in PVD glasses of toluene,[44] and the temperature window above is a reasonable estimate of the regime where secondary relaxations might contribute to the heat capacity of the liquid-cooled glass of ethylbenzene.[45] Accounting for this difference in heat capacity, Yamamuro et al.'s value of T_K is lowered by 0.7 K, to just above 100 K. Our recalculation of T_K clearly makes a significant assumption that could be tested with heat capacity measurements on PVD glasses over a wide temperature range.

One potential criticism of PVD glasses serving as models for the supercooled liquid is that deposited glasses can be anisotropic.[42, 46-48] Thus, the birefringence of these PVD glasses (also obtained from ellipsometry) provides a further test of the extent to which the as-deposited films have the structure expected for the supercooled liquid. Birefringence values for glasses deposited at all substrate temperatures and deposition rates are shown in Figure 6. For substrate temperatures above 109 K, all the as-deposited glasses are isotropic within measurement error. At lower substrate temperatures, the glasses are birefringent, with the maximum value equal to 0.02. In this regime, as the deposition rate is lowered, the birefringence values decrease significantly. This behavior supports the view that PVD glasses approach the isotropic structure of the supercooled liquid in the limit of low deposition rates.

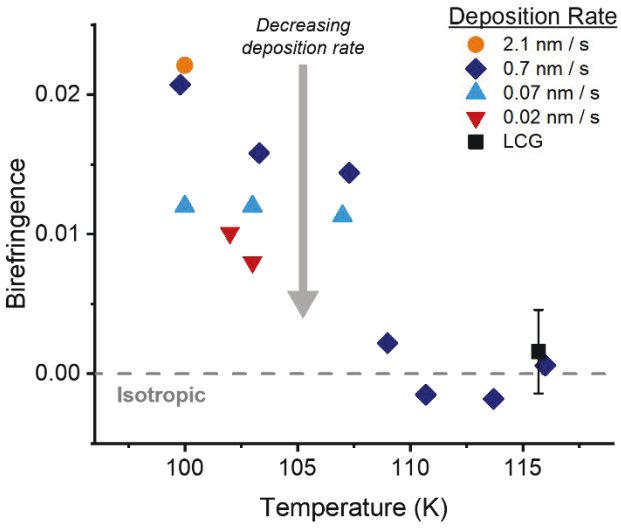


Figure 6. Birefringence as a function of substrate temperature for vapor-deposited glasses of ethylbenzene, with deposition rates indicated in the legend. The black open square is the average birefringence of all glasses prepared by cooling the liquid at 5 K/min; the error bar indicates one standard deviation. Error bars for the PVD glasses are expected to be comparable.

The results presented here are significant in establishing that PVD glasses can be useful models for the equilibrium supercooled liquid. We have shown that the density and refractive index values obtained in the limit of low deposition rates are consistent with those expected for the supercooled liquid down to 103 K. By combining our results with previous measurements, we show that the density, refractive index, and enthalpy of PVD ethylbenzene glasses all have the values expected for the equilibrium supercooled liquid down to 105 K. While the glasses obtained at 103 K are mildly anisotropic, those prepared at the lowest deposition rate are substantially more isotropic than those prepared at higher deposition rates. These results, taken together, strongly suggest that the properties of the supercooled liquid, obtained by extrapolation from above T_g, are accurate down to a few Kelvin above T_K.

These new results on PVD glasses provide insight into the resolution of the Kauzmann entropy crisis. At some point, the extrapolation of the supercooled liquid entropy must fail. Prior to work on PVD glasses, we understood that the entropy crisis for ethylbenzene should somehow be resolved between T_g (116 K) and T_K (~101 K). As one extreme, the extrapolation might fail gradually as the temperature is lowered below T_g with continuously larger deviations between the actual supercooled liquid properties and those obtained by extrapolation. At the opposite extreme, the extrapolation might fail at the lowest possible temperature (T_K) via a phase transition. The results presented here on PVD glasses of ethylbenzene, in combination with those from ref [33], establish with reasonable certainty that the extrapolated properties of the supercooled liquid of ethylbenzene are accurate down to within a few Kelvin of T_K. For this system, the entropy crisis is not resolved by a gradual failure of the high-temperature extrapolation as temperature is lowered. Rather, the properties of the supercooled liquid must adjust fairly abruptly below 103 K, either continuously or via a phase transition. Thus, these experiments on PVD glasses substantially increase the likelihood of a phase transition to the ideal glass of ethylbenzene at the Kauzmann temperature. It is possible that other liquids may resolve the entropy crisis differently; for example, systems exhibiting polyamorphism may undergo a liquid-liquid transition instead.

Based on results in the literature, PVD is most likely to access equilibrated states close to T_K for low molecular weight systems without hydrogen bonding.[49] In order to test the generality of the results presented here for ethylbenzene, it would be useful for future experiments utilizing low deposition rates to study toluene as there is evidence from calorimetry[34, 37] that glasses with fictive temperatures close to T_K can also be prepared for this system.

Methods: Ethylbenzene glasses were prepared by PVD in a vacuum chamber described previously.[50-52] Ethylbenzene was obtained from Sigma Aldrich (anhydrous, 99.8% purity) and used without further purification. The molecules are introduced into the vacuum chamber (base pressure ~ 10^{-9} torr) via a fine leak valve. All films deposited were about 400 nm thick.

For *in situ* ellipsometry measurements, ethylbenzene molecules are deposited directly onto a 1" silicon wafer with a 25 nm oxide layer. The silicon wafer is in thermal contact via indium foil with a copper finger cooled by nitrogen gas. The copper finger houses a platinum RTD (resistance temperature detector) and a cartridge heater that are used to control the temperature of the silicon wafer in conjunction with a Lakeshore 340 temperature controller. Due to imperfect thermal contact between the copper finger and the silicon wafer, a correction of 3-4 K was applied to obtain the temperature of the PVD glass on the silicon wafer. We use the T_g value obtained upon heating the liquid-cooled glass (cooling and heating both at 5 K/min) as our reference temperature. Based upon dielectric relaxation measurements, Chen et al.[35] report that the structural relaxation time has a value of 100 s at 115.7 K and we use this value for T_g for the glass prepared by cooling at 5 K/min. All the liquid-cooled glasses discussed in this paper were prepared by cooling at 5 K/min except for one data set shown in Figure 3 (cooled at 0.5 K/min).

Ellipsometry measurements were performed using a J. A. Woollam M-2000U ellipsometer with an incident angle of 70°. The ellipsometric data were analyzed using an anisotropic Cauchy model to describe the organic layer and fit in the wavelength range of 350 – 1000 nm. The Cauchy model is shown in Equation (2) and has been used previously for anisotropic organic films[42].

$$n_o(\lambda) = A_o + \frac{B}{\lambda^2}; n_e(\lambda) = A_e + \frac{B}{\lambda^2} \quad (2)$$

During the heterogeneous transformation[42] of vapor-deposited glasses (from 123 to 125 K in Figure 2), this model is not adequate to quantitatively describe the data; this has no impact on Figures 4 or 5, or our conclusions.

Ellipsometry data was obtained during heating at 5 K/min and was fit following the procedure outlined in 2001 by Dalnoki-Veress et al.[53] using the function described by Equation (3):

$$h(T) = w\left(\frac{M-G}{2}\right)\ln\left[\cosh\left(\frac{T-T_g}{w}\right)\right] + (T-T_g)\left(\frac{M+G}{2}\right) + c \qquad (3)$$

This fit results in the values of T_{onset} for the as-deposited glass and the value of T_g for the liquid-cooled glass. The fit also provides the "h_0" value used to normalize the data in Figure 3. To obtain the fictive temperatures for both the thickness and refractive index data, the high-temperature linear portion of the fit to the supercooled liquid data was extended to intersect with the fit for the as-deposited glass, similar to the procedure in Reference [54]. Sample fits are provided in the Supporting Information. Vertical error bars in Figures 4 and 5 represent the error in the determination of the fictive temperature due to the uncertainty in fitting equation (3). Horizontal error bars in Figure 5 represent the uncertainty in the temperature. Note that our ellipsometry measurements were not used to determine absolute densities; the density of the as-deposited glass relative to the liquid-cooled glass allows the determination of T_f.

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Supporting Information

Sample fits of ellipsometry data to the model of Dalnoki-Veress et al.[53].

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Supporting information: Vapor-Deposited Ethylbenzene Glasses Approach "Ideal Glass" Density

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Fits of ellipsometry data

In Figure S1 we provide an example showing the fitting procedure used with ellipsometry data obtained during temperature-ramping. The figure shows thickness and refractive index data obtained as the temperature is increased for the same data set shown in Figure 2 of the main text. We fit the data to an equation (S1) described by Dalnoki-Veress et al.[53]

$$h(T) = w\left(\frac{M-G}{2}\right)\ln\left[\cosh\left(\frac{T-T_g}{w}\right)\right] + \left(T-T_g\right)\left(\frac{M+G}{2}\right) + c \qquad (S1)$$

This procedure is intended to eliminate potential bias associated with manually extracting T_g and T_{onset} values.

Figure S1 illustrates that Equation S1 fits the data well except for the transformation of the as-deposited glass into the supercooled liquid, between 123 K and 125 K. (The non-monotonic behavior displayed in the data over this 2 K range is indicative of transformation via a growth front. The rest of the fit is not affected.) The arrows in Figure S1 indicate the meaning of the values extracted from the fit for T_g, T_{onset}, and h_0. T_g is the glass transition temperature for the liquid-cooled glass, obtained upon heating; T_{onset} is the beginning of the transformation for the PVD glass; h_0 is the thickness at T_g and is used to normalize the y-axis data in Figure 3. The temperature axis in Figure S1 has been corrected by subtracting the difference between the fitted value of T_g and the reference T_g value of 115.7 K. (See methods for details.)

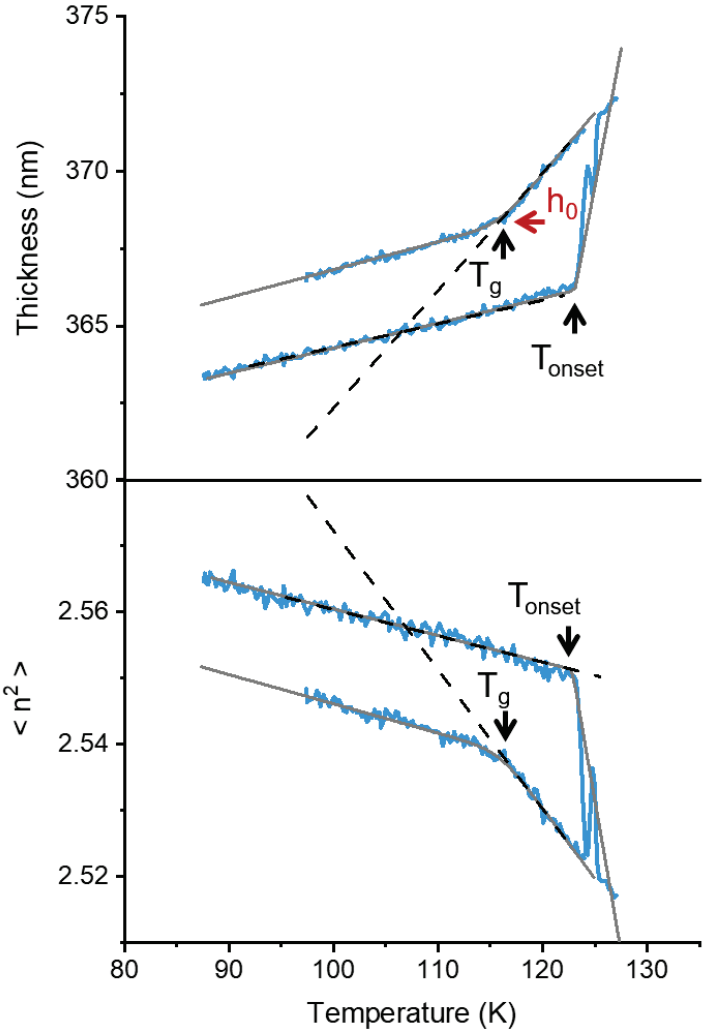

Figure S1. Fits of equation S1 to the heating curves for the as-deposited glass and the liquid-cooled glass for the data presented in Figure 2 of the main text. The blue lines are the thickness and refractive index data, the grey lines are the fits to equation S1, and the black dashed lines are linear extrapolations of the fits to the supercooled liquid data. The intersection between the supercooled liquid extrapolation and the glass data defines the fictive temperature T_f. Arrows indicate values that are extracted from the fits to equation S1.