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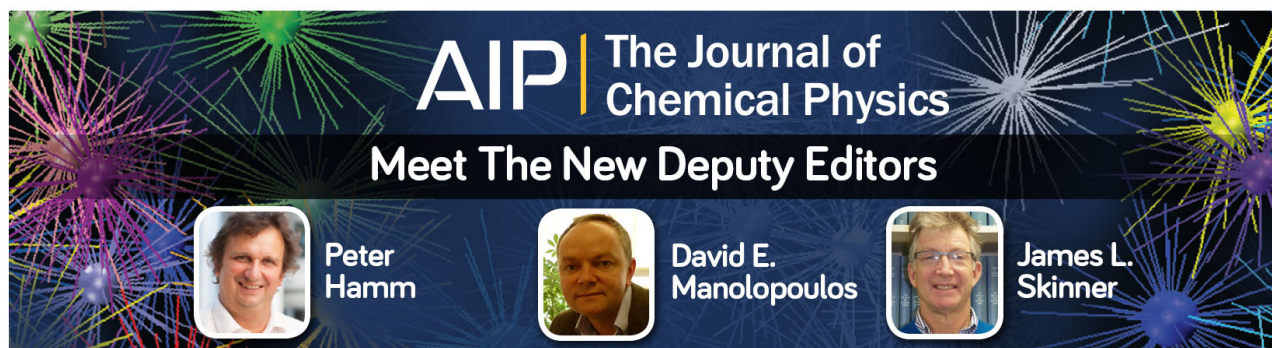
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How much time is needed to form a kinetically stable glass? AC calorimetric study of vapor-deposited glasses of ethylcyclohexane

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Glasses of ethylcyclohexane produced by physical vapor deposition have been characterized by *in situ* alternating current chip nanocalorimetry. Consistent with previous work on other organic molecules, we observe that glasses of high kinetic stability are formed at substrate temperatures around $0.85 T_g$, where T_g is the conventional glass transition temperature. Ethylcyclohexane is the least fragile organic glass-former for which stable glass formation has been established. The isothermal transformation of the vapor-deposited glasses into the supercooled liquid state was also measured. At seven substrate temperatures, the transformation time was measured for glasses prepared with deposition rates across a range of four orders of magnitude. At low substrate temperatures, the transformation time is strongly dependent upon deposition rate, while the dependence weakens as T_g is approached from below. These data provide an estimate for the surface equilibration time required to maximize kinetic stability at each substrate temperature. This surface equilibration time is much smaller than the bulk α -relaxation time and within two orders of magnitude of the β -relaxation time of the ordinary glass. Kinetically stable glasses are formed even for substrate temperatures below the Vogel and the Kauzmann temperatures. Surprisingly, glasses formed in the limit of slow deposition at the lowest substrate temperatures are not as kinetically stable as those formed near $0.85 T_g$. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4906806>]

I. INTRODUCTION

Glassy films prepared by physical vapor deposition at substrate temperatures close to the glass transition temperature T_g can exhibit extraordinary features, which include high kinetic stability demonstrated by a delayed transformation into the supercooled liquid state. Furthermore, vapor-deposited glasses have lower enthalpy, lower specific volume, and lower heat capacity than the ordinary liquid cooled glass made of the same material.^{1–5} In many respects, these vapor-deposited glasses have properties that would be expected if ordinary glasses were aged over thousands or millions of years. A number of small organic molecules which form extraordinary kinetically stable glasses by vapor deposition have been investigated, e.g., $\alpha\alpha\beta$ -trisinaphthylbenzene (TNB),⁴ indomethacin (IMC),⁴ *cis/trans*-decalin,⁶ toluene,^{7,8} ethylbenzene,^{8–10} isopropylbenzene, propylbenzene,¹¹ nifedipine, felodipine, phenobarbital,¹² and celecoxib.¹³

These glasses of high kinetic stability are thought to form because of enhanced mobility at the surface during vapor deposition. When a molecule is deposited onto the surface of a growing glass film, it becomes part of a mobile surface layer, provided that the temperature of the substrate is not too low. The molecules near the surface have the mobility to rearrange to reach more efficient packing configurations, before being buried and becoming part of the bulk glass by further deposition. The substrate temperature yielding maximal stability, often around $0.85 T_g$, can be viewed as a compromise between molecular mobility at the free surface (which decreases with decreasing temperature) and the

driving force towards deep states within the energy landscape (which increases with decreasing temperature).³ If a sample is deposited at temperatures far below T_g , unstable glasses are formed, as investigated by Suga *et al.*, presumably because the surface is essentially immobile on the time scale of deposition.¹⁴

A number of experiments support the idea that highly stable glasses are formed because of highly mobile surfaces. If this mechanism is correct, then depositing at lower rates will give molecules more time to equilibrate at the surface, resulting in packing arrangements with lower energies and higher barriers to rearrangement. Furthermore, at a given temperature, lowering the deposition rate beyond some value should have no further impact on glass properties because the surface should reach a structure corresponding to a metastable state different from the crystal. Published data are consistent with these ideas but do not fully test them. Most of the published work falls into one of three categories. One group of studies has utilized relatively high substrate temperatures (above $0.9 T_g$) and report that the deposition rate has little or no effect on glass properties.^{8,10} These results are broadly consistent with an equilibrated surface over the tested range of deposition rates. Particularly notable in this group is the work of Ahrenberg *et al.*, in which toluene glasses were vapor-deposited on $0.90 T_g$ at rates from 50 nm s^{-1} to 0.02 nm s^{-1} .⁸ A second group of studies utilized relatively low substrate temperatures (at or below $0.85 T_g$) and report that lower deposition rates result in glasses with increased kinetic stability.^{15–17} None of these studies clearly identify a limiting deposition rate beyond which glass properties do not change.

These results are consistent with the idea that even lower deposition rates would result in a fully equilibrated surface. For example, Ishii *et al.* report that decreasing the deposition rate from 20 nm s^{-1} to 0.3 nm s^{-1} significantly increased the stability of ethylbenzene glasses deposited at $0.68 T_g$.¹⁷ The third group of studies explored the impact of deposition rate at more than one substrate temperature.^{2,18} These results are also consistent with the hypothesis that surface mobility allows the formation of kinetically stable glasses, but only allow the identification of the limiting deposition rate at a single substrate temperature. For example, Dawson *et al.* vapor-deposited indomethacin and concluded that deposition at rates lower than 7 nm s^{-1} does not increase kinetic stability as long as the substrate temperature is above $0.92 T_g$.¹⁸ Recent computer simulations of vapor-deposited alkanes by Lin *et al.* are conceptually similar to this experimental work.¹⁹ We note that other experiments (not involving vapor deposition) have directly observed that molecular glasses have highly mobile surfaces at temperatures just below T_g , and theoretical models support this idea.^{20–24}

The above summary makes clear the opportunity for a study that utilizes a wide range of deposition rates and includes the temperature range below $0.85 T_g$. There are serious questions as to what state should result from surface equilibration at low temperatures. The configurational entropy of many supercooled liquids goes to zero (by extrapolation) at a temperature denoted as the Kauzmann temperature T_K , typically in the range of 0.7 – $0.85 T_g$. In the same temperature range, the main relaxation time of a supercooled liquid apparently diverges (again by extrapolation) at a temperature T_0 . These two observations are often interpreted to indicate that supercooled liquids do not exist at lower temperatures. If this was the case, then deposition at very low rates below T_K and T_0 could not produce the supercooled liquid but might produce an “ideal glass.”

A particularly useful method of investigation of vapor-deposited glasses is alternating current (AC) chip calorimetry. This nanoscale calorimetry technique can be used to study directly the dynamics of the molecular processes of thin films down to few nanometers.^{25,26} AC nanocalorimetry has previously been used to characterize highly kinetically stable vapor-deposited glasses.^{4,8,27} From temperature scanning measurements, one obtains the reversing heat capacity and the onset temperature for the transition of the as-deposited (AD) glass into the supercooled liquid, which gives information about the molecular packing of the system and quantifies the kinetic stability. AC nanocalorimetry also allows a more precise characterization of kinetic stability by monitoring the transformation of the as-deposited glass to the supercooled liquid in quasi-isothermal conditions.^{1,8}

In this paper, we investigate the kinetic stability of vapor-deposited glasses of ethylcyclohexane with AC chip calorimetry. The deposition temperatures range from T_g down to well below $T_K \approx T_0$. Ethylcyclohexane is a good glass-former and considerable information is already available about its supercooled liquid and liquid-cooled glass. Dielectric relaxation has been used to study the α - and β -relaxations (primary and secondary relaxations)²⁸ and adiabatic calorimetry has been used to obtain heat capacity

for the different states in a wide temperature range.^{29–31} There has been some controversy regarding whether or not ethylcyclohexane can form kinetically stable glasses via vapor deposition.^{32,33} Ethylcyclohexane is one of the least fragile organic liquids (with the kinetic fragility $m \approx 56$) and some authors have concluded that glasses of high kinetic stability can only be formed from very fragile liquids.^{34,35}

We find that ethylcyclohexane forms glasses of high kinetic stability when vapor-deposited at substrate temperatures near $0.85 T_g$. This result is consistent with recent experiments indicating that glasses of high kinetic stability can be formed across the entire range of fragilities exhibited by organic liquids.³⁶ At seven different substrate temperatures, we determined the kinetic stability of glasses formed from deposition rates covering four orders of magnitude. From these results, we are able to estimate the surface equilibration time needed to maximize kinetic stability at each substrate temperature. The surface equilibration time is much smaller than the bulk α -relaxation time and similar (within two orders of magnitude) to the β -relaxation time of the ordinary glass. Kinetically stable glasses are formed even for substrate temperatures below T_K and T_0 . Surprisingly, the kinetic stability of glasses in the limit of low deposition rate *decreases* with substrate temperature below $0.85 T_g$.

II. EXPERIMENTAL

A. AC calorimetry and vapor deposition

The vapor deposition chamber is schematically illustrated in Figure 1(a). The vacuum system is very similar to the apparatus described previously.^{8,37}

In situ differential AC chip calorimetry was used to characterize the vapor-deposited glassy samples.^{25,26,37} Two pairs of sensors are located in the calorimeter cell; one pair can be utilized for fast-scanning calorimetry measurements and another pair for AC calorimetry measurements, as shown in Figure 1(b). Each pair of sensors has a sample sensor for direct deposition of a sample and a reference sensor, which is inside the calorimeter cell protected from deposition. The calorimeter cell was cooled with a closed cycle helium cryostat, Model CH-204SN, Cold Edge Technologies, USA, that reaches temperatures down to 10 K. The sensors XI39390 (Figure 2) used for the measurements in this work are chip-nanocalorimeters fabricated by Xensor Integrations, NL.³⁸ The sensors are coated with SiO_2 , thus this is the substrate material. Fast-scanning calorimetry measurements are still in progress and will not be presented here.

The AC calorimeter is similar to that described elsewhere.^{25,37} Oscillating power was applied to the inner heater of the sensor and the amplitude and phase angle of the complex differential thermopile signal were measured by a digital lock-in amplifier (Model 7260, EG&G, USA). The complex differential thermopile signal, between sample and reference sensors, quantifies the sample heat capacity (J K^{-1}). For all measurements, we subtracted a background measurement (where the sample sensor is empty) in the complex plane, in order to correct for small differences between the sensors. We present these baseline subtracted thermopile data as heat capacity in arbitrary unit (a.u.).

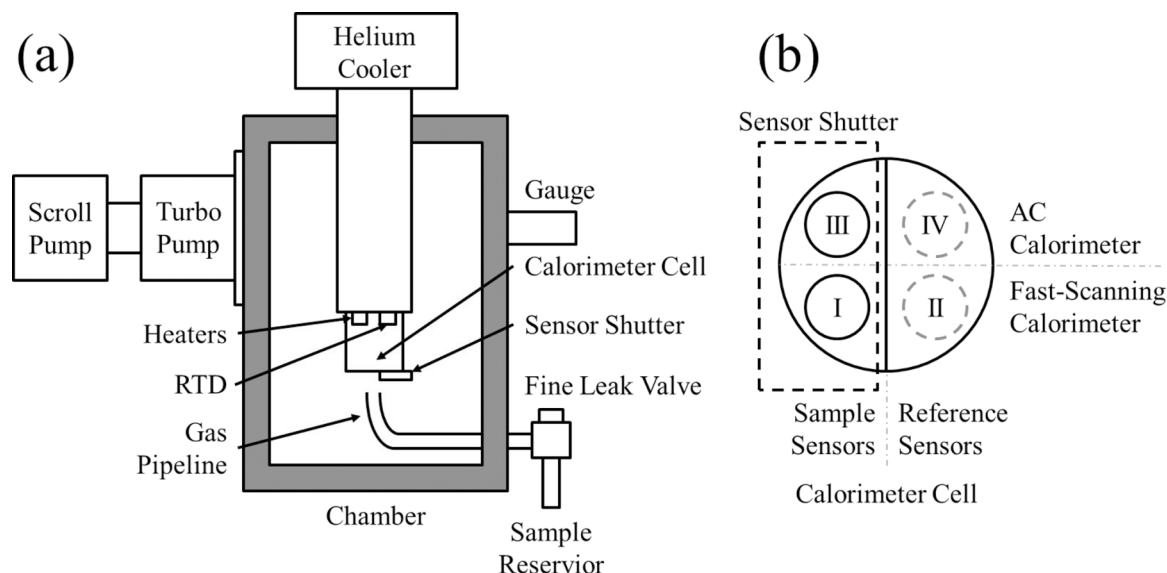


FIG. 1. Schematic of (a) vapor deposition chamber and (b) calorimeter cell. The sensor shutter is shown as the dashed rectangle, which can be slid over and fully cover the sample sensors.

We did not perform further corrections because the relation between the corrected thermopile signal and the reversing heat capacity of the sample is complex.^{25,37,39} Therefore, in some cases, the curves are tilted, resulting in unphysical negative slopes. However, this does not affect the analysis in this paper and the use of the corrected thermopile data is sufficient for our purpose. Reversing heat capacity does not provide sufficient information to derive thermodynamic potentials such as enthalpy, but does provide information about kinetic stability as discussed below.

Before deposition and during the AC calorimetric measurements, the base pressure in the chamber was below 2×10^{-8} millibars. This ensured little co-deposition of water or other substances even for the lowest deposition rates. At the base pressure and a substrate temperature of 60 K, the co-deposition rate was of the order of 0.2 pm s^{-1} , which is 10% of the lowest rate employed (2 pm s^{-1}) and thus cannot be fully neglected. At the start of deposition, the sensor shutter, Figure 1(b), uncovered the sample sensors. The deposition rates from 50 nm s^{-1} down to 0.002 nm s^{-1} were controlled by adjusting the fine leak valve, which is connected to the sample reservoir. The material in the sample reservoir is directed into the chamber through a gas pipeline, without additional heating necessary as the vapor pressure of the sample material is high

at ambient temperature. The gas pipeline is located about 5 cm under the calorimeter cell, in order to ensure mostly direct deposition and that both sample sensors are exposed to equal deposition. After the deposition, the sensor shutter recovered the sample sensors, to ensure no additional deposition during the measurements. This also allowed the deposition to be immediately started or stopped without adjusting the fine leak valve. By monitoring the pressure in the chamber during deposition, the deposition rate was controlled and ensured to be constant throughout the deposition process. The deposition rate was estimated from the measured thermopile signal according to the procedure described in Ref. 37. Even at the highest deposition rates, the pressure in the chamber was always below 10^{-4} millibars and the mean free path of the molecules was at least one order of magnitude larger than the distance between the pipe and the sensor. Therefore, it is unlikely that molecules experienced collisions and clustering on the way to the substrate. The resistance of the membrane heater was employed as a thermometer during the depositions. Temperature increase during deposition was below 0.5 K and is negligible.

For temperature calibration, the frequency dependence of the dynamic glass transition temperature of toluene and ethylbenzene was measured. A sample with ca. 400 nm film

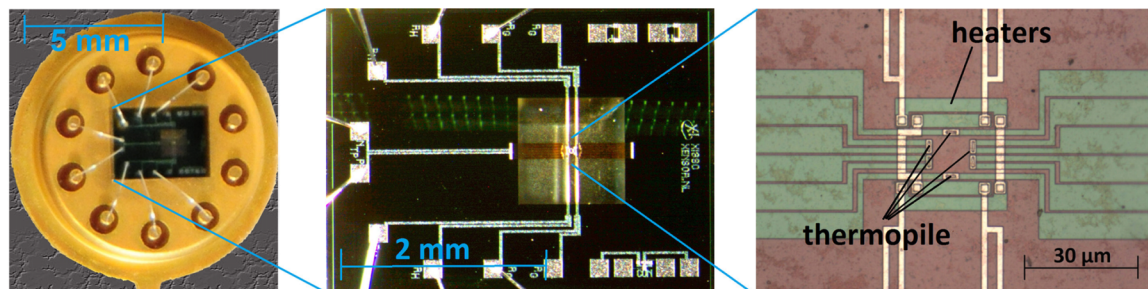


FIG. 2. Images of the chip-nanocalorimeters, XI39390, at three different magnifications. (Left) Chip mounted on TO-5 housing; (middle) the chip; (right) the central part, including the active area with the inner and outer heaters, the six hot junctions of the thermopile, and the conducting stripes. Reprinted with permission from Ahrenberg *et al.*, Rev. Sci. Instrum. **83**, 033902 (2012). Copyright 2012, AIP Publishing LLC.

thickness was deposited onto the chip sensor at 105 K and scanned slightly above its glass transition to fully transform the sample to an ordinary liquid. This is done to erase all memory regarding the deposition process before cooling down to about 110 K at 0.67 K min^{-1} . The temperature range of measurement was chosen such that crystallization and sublimation of the sample were avoided. After the transformation scan, the subsequent scans were done with different frequencies ranging from 4 Hz to 8 kHz. For every measured frequency, the position of the minimum of the phase angle is determined as the corresponding dynamic glass transition temperature, $T_{g,dyn}$. The corresponding dynamic glass transition temperatures at different frequencies across the temperature range from 120 K to 130 K were compared to the known dynamic glass transition temperatures from Vogel-Fulcher-Tammann (VFT) parameters, described previously.⁸ For calibration at lower temperatures, a similar frequency dependent experiment was performed with 1-pentene. Since no VFT parameters for the α -relaxation of 1-pentene are available in the literature, the obtained frequency dependent calorimetric $T_{g,dyn}$ were fit to the VFT equation (Eq. (1)) and the extrapolated value at $\tau = 100 \text{ s}$ was compared to the expected value from adiabatic calorimetry ($T_g = 70 \text{ K}$ from Ref. 40). Finally, an uncertainty of temperature of $\pm 1 \text{ K}$ for the temperature range from 60 to 140 K was obtained.

B. Materials

Ethylcyclohexane was purchased from Acros Organics and was used without further purification. The chemical purity was better than 99%. The glass transition temperature of ethylcyclohexane from dielectric spectroscopy is known to be 100 K when $\tau(T_g) = 100 \text{ s}$.²⁸ Adiabatic calorimetry of ethylcyclohexane glass gives a T_g of 104.5 K.³¹ We will use the 100 K temperature for T_g in this work. The temperature dependent behavior of the dielectric relaxation time $\tau_\alpha = 1/(2\pi\nu_{peak})$ is well described by a VFT equation

$$\log(\tau_\alpha) = A + \left(\frac{B}{T - T_0} \right), \quad (1)$$

with $A = -13.7$, $B = 397 \text{ K}$, $T_0 = 75.5 \text{ K}$.⁴¹ The fragility of ethylcyclohexane is reported as $m = 56.5$, which is less fragile than other organic liquids that have been shown to form stable glasses.²⁸ The secondary β -relaxation of ethylcyclohexane shows an Arrhenius temperature dependence. The temperature dependence of $\log(\tau_\beta)$ can be described by Eq. (1) with $A = -12.9$, $B = 949 \text{ K}$, and $T_0 = 0 \text{ K}$ (see Figure 11 below).

The frequency dependence of the calorimetric dynamic glass transition temperatures of ethylcyclohexane was measured with the same method and conditions as for toluene and ethylbenzene. The corresponding dynamic glass transition temperatures are shown in the relaxation map in Sec. IV, Figure 11 as open red stars. We found that the VFT equation for dielectric data from Mandanici *et al.* is consistent with our AC calorimetric data within $\pm 1 \text{ K}$.⁴¹

Figure 3(a) shows the specific heat capacity measured with quasi-adiabatic calorimetry for the glassy state,³¹ and with adiabatic calorimetry for crystal and liquid states.²⁹ The glass obtained by slow cooling the liquid (about -0.1 K/min)

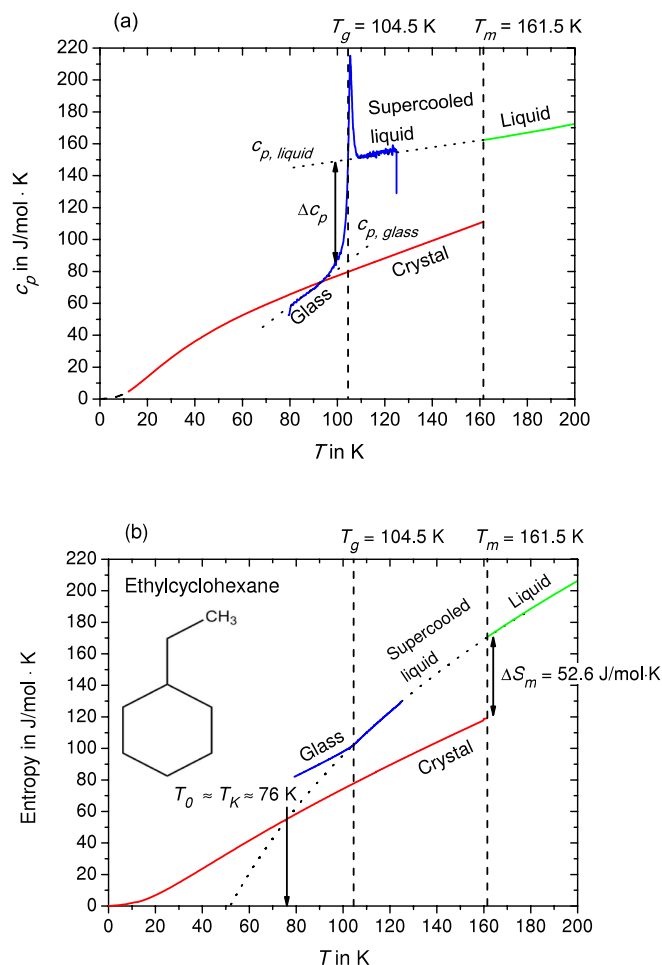


FIG. 3. (a) Specific heat capacity curves measured for ethylcyclohexane with quasi-adiabatic calorimetry for glassy state (blue) were provided by the authors of Ref. 31, and with adiabatic calorimetry for crystal (red), which was extrapolated down to zero (black, dashed), and liquid (green), which was interpolated to the supercooled liquid,²⁹ and further linearly extrapolated to 60 K (black, dotted). (b) Entropy curves for the liquid, crystal, and ordinary glass states. Molecular structure of ethylcyclohexane is also included as inset.

exhibits a peak (overshoot) at the glass transition, because the heating rate is faster than the glass forming cooling rate. The glass transition temperature (half step temperature) of $T_g = 104.5 \text{ K}$ is slightly higher than the $T_g = 100 \text{ K}$ value obtained from dielectric spectroscopy when $\tau(T_g) = 100 \text{ s}$.²⁸ We are using the $T_g = 100 \text{ K}$ value in this paper.

The data in Figure 3(a) can be used to obtain the entropies of crystal, liquid, and glass states shown in Figure 3(b). The specific heat capacity of the crystal state in Figure 3(a) was extrapolated down to zero (solid red curve with dashed black line down to zero). The specific heat capacity between the liquid state (solid green curve) and the supercooled liquid state (blue line) was linearly interpolated and further extrapolated linearly down to 60 K (dotted black line). In order to get the entropies, the specific heat capacities of crystal, liquid, and glass states were divided by corresponding temperatures and integrated. The curve for the liquid was integrated from 60 K to 200 K and adjusted at the melting temperature to the entropy curve of the crystal by the known entropy of melting, $\Delta S_m = 52.6 \text{ J/mol K}$, which is obtained using the enthalpy of melting $\Delta H_m = 8.5 \pm 0.3 \text{ kJ/mol}$ at the melting temperature,

$T_m = 161.5$ K.³¹ The temperature of intersection of the entropy of the extrapolated liquid state with the entropy of the crystal state is denoted as the Kauzmann temperature $T_K \approx 76$ K, which agrees with the Vogel temperature $T_0 = 75.5$ K from the VFT fit in Figure 11.

III. RESULTS

A. Stability of as-deposited glasses

In this work, AC nanocalorimetry was used to quantify the kinetic stability of vapor-deposited glasses of ethylcyclohexane. Glasses were deposited over a range of substrate temperatures and deposition rates in order first to determine the conditions that yield the most kinetically stable vapor-deposited glasses.

Figure 4 shows the heat capacity and phase angle curves obtained by heating the as-deposited glasses. As described in Ref. 3, there are two characteristics of the heat capacity curves that can be used to quantify the stability: the heat capacity of the as-deposited glass and the onset temperature for the transformation of the as-deposited glass into the

supercooled liquid. For the experiments shown in Figure 4, the experimental parameters are as follows: 2 nm s^{-1} deposition rate, 0.67 K min^{-1} heating/cooling rate, sample thickness ca. 400 nm , and 20 Hz thermal oscillation.

The onset temperature T_{onset} is defined as the intersection of the extrapolated glassy line and the tangent of the transformation from glassy state to supercooled liquid state. At T_{onset} , the molecules have sufficient energy to surmount the barriers imposed by stable glass packing. This allows transformation into supercooled liquid, and an increase in heat capacity is observed as a consequence of configurational sampling. On the contrary, the molecules remained immobile below T_{onset} .

The fractional C_p decrease is utilized to characterize the difference in heat capacity between as-deposited and ordinary glasses (OG),⁸

$$\text{Fractional } C_p \text{ decrease} = 1 - \frac{C_p(\text{AD})}{C_p(\text{OG})}. \quad (2)$$

The fractional C_p decrease for ethylcyclohexane was calculated at 95 K , which is $T_g - 5 \text{ K}$. This temperature is low enough to ensure that we were directly comparing the solid-state properties of the as-deposited and ordinary glasses. For these comparisons, the ordinary glasses were prepared by cooling the supercooled liquid at 0.67 K min^{-1} .

For each as-deposited glass, the onset temperature and fractional C_p decrease were determined and assembled in Figure 5. When the substrate temperature $T_{\text{substrate}}$ is above the conventional glass transition temperature T_g , an ordinary glass is deposited and the apparent “onset” temperature of the glass transition determined by the tangent construction is 8 K below $T_{g,\text{dyn}}$. For lower substrate temperatures, the onset temperature reaches a maximum for substrate temperatures from $0.8 T_g$ to $0.9 T_g$; this is consistent with many other organic molecules that form kinetically stable glasses. For the substrate temperature lower than $0.7 T_g$, the onset temperature decreases below the conventional glass transition T_g , indicating the formation of unstable as-deposited glasses at the deposition rate of 2 nm s^{-1} . A higher T_{onset} signifies an increase in kinetic

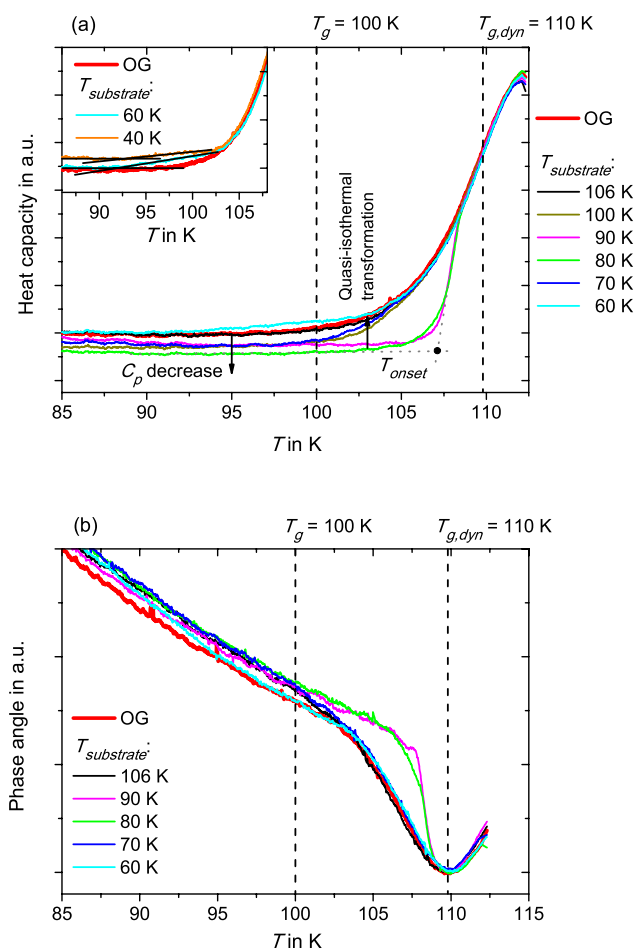


FIG. 4. (a) Heat capacity and (b) phase angle of as-deposited glasses of ethylcyclohexane deposited at different substrate temperatures ranging from 60 K to 106 K at a deposition rate of 2 nm s^{-1} . A heating curve corresponding to an OG is shown for comparison. The determinations of the C_p decrease and T_{onset} are also shown. For studying the influence of deposition rate on the kinetic stability of the glasses, the quasi-isothermal transformations were measured at transformation temperature of 103 K as indicated.

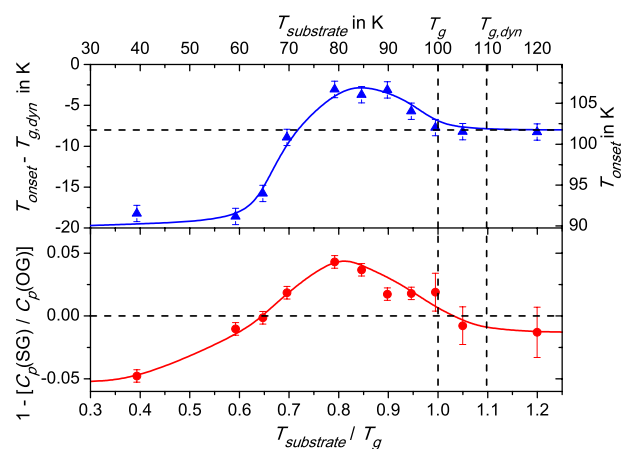


FIG. 5. (a) Onset temperature (T_{onset}) and (b) fractional C_p decrease of ethylcyclohexane, determined from Eq. (2), as a function of substrate temperature during deposition. All glasses shown were prepared at a deposition rate of 2 nm s^{-1} .

stability, because higher temperatures are required to dislodge the molecules from their glassy configuration to transform into the supercooled liquid.⁴

The fractional C_p decrease follows a similar trend as the onset temperature. At substrate temperatures close to T_g , as-deposited glasses do not exhibit a detectable heat capacity decrease, which means these glasses are indistinguishable from a liquid-cooled glass. The C_p reaches its maximum decrease (about 3.5% as compared to the ordinary glass) at substrate temperatures from $0.8 T_g$ to $0.9 T_g$. The drop in the heat capacity is presumably associated with a shift in the vibrational density of states as a result of efficient packing. For substrate temperatures below this range, the heat capacity decrease disappears and finally an increase in heat capacity is observed at the lowest substrate temperatures.

For comparison between the as-deposited glasses (first heating) and ordinary glasses (second heating), all measured second heating curves were scaled with a factor determined in the glassy state at 95 K. This scaling allows the glassy C_p of the different stable glasses to be compared even though the absolute heat capacity values are not known and may differ slightly due to different film thicknesses.⁸

B. Quasi-isothermal transformation experiments

AC calorimetry allows for the observation of the quasi-isothermal transformation from the kinetically stable glass to the supercooled liquid at temperatures a few Kelvin above T_g .^{8,15,42} These quasi-isothermal transformation experiments provide a direct study of the kinetic stability of the glasses. The heat capacity of the kinetically stable glass is lower than that of the supercooled liquid slightly above T_g , as shown in Figure 4(a) by the vertical arrow at 103 K. In the quasi-isothermal transformation experiments, the heat capacity is observed to slowly increase from the stable glass value to the supercooled liquid value at the transformation temperature, which is higher than the conventional glass transition temperature.

Isothermal transformations were performed at different transformation temperatures $T_{\text{transform}}$. For these experiments, the substrate temperature $T_{\text{substrate}} = 85$ K, the thickness of ca. 400 nm, the 20 Hz thermal oscillation, and the deposition rate of 8 nm s^{-1} were kept constant. After deposition, the sample temperature was increased to the transformation temperature $T_{\text{transform}}$ with heating rate of 0.67 K min^{-1} . $T_{\text{transform}}$ was varied by ~ 0.4 K increments and the lowest $T_{\text{transform}}$ was 1.5 K above T_g . Figure 6 shows the increase of heat capacity during the isothermal transformation from as-deposited glasses of high kinetic stability to supercooled liquids for different transformation temperatures. The transformation time $t_{\text{transform}}$ is denoted as the time needed for the as-deposited kinetically stable glasses to complete transformation into an ordinary liquid. It is determined by a tangent construction as indicated in Figure 6.

As has been previously discussed, when a kinetically stable glass is heated above T_g , a mobility front (the supercooled liquid) initiates at the free surface and propagates into the stable glass at constant velocity.^{1,43–45} For thin films, transformation by a growth front results in a linear increase

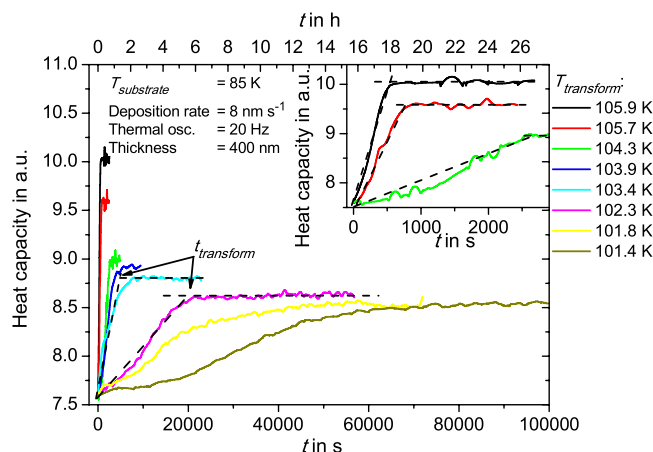


FIG. 6. The increase in heat capacity during isothermal transformation from the as-deposited kinetically stable glass to the supercooled liquid at the indicated $T_{\text{transform}}$.

of heat capacity with time.⁴⁶ Figure 6 shows qualitative agreement with such a linear transformation behavior for high transformation temperatures. At the two lowest transformation temperatures, there is some deviation from linearity which may indicate an additional transformation process initiated within the bulk.⁴⁶ As discussed by Kearns *et al.*,⁴⁶ there is a certain probability to initiate transformation within the bulk if the growth front from the surface does not transform a given volume in a short enough time. In previous work, this occurred with increasing film thickness, i.e., the time needed for the transformation initiated from the surface becomes too long. Here, we increase the transformation time by reducing transformation temperature and it is possible that a bulk mechanism similarly comes into play.

In Figure 7, the logarithm of the ratio $t_{\text{transform}}/\tau_\alpha$ is plotted versus the negative of logarithm τ_α . For the y-axis, the transformation time $t_{\text{transform}}$ was normalized by

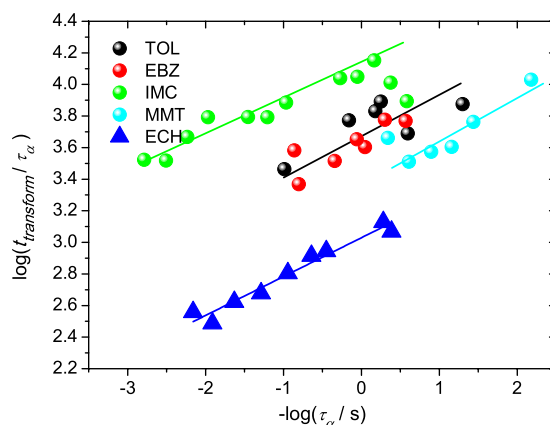


FIG. 7. The isothermal transformation time $t_{\text{transform}}$, normalized by the structural relaxation time τ_α , as a function of τ_α for ethylcyclohexane (ECH; blue triangles). The substrate temperature, deposition rate, and thickness of the ethylcyclohexane glasses were kept constant as 85 K, 8 nm s^{-1} , and 400 nm, respectively. Also included for comparison are results for other substances deposited at the given rates (full circles): toluene at 2 nm s^{-1} (TOL; black),⁸ ethylbenzene at 2 nm s^{-1} (EBZ; red),⁸ methyl-*m*-toluate at 0.2 nm s^{-1} (MMT; cyan),³⁶ and indomethacin at 0.2 nm s^{-1} (IMC; green).⁴⁷ and at comparable substrate temperatures ca. $0.85 T_g$ and thickness ca. 400 nm.

the structural relaxation time τ_α to highlight the much longer transformation times compared to τ_α . For the x-axis, the transformation temperature $T_{\text{transform}}$ was replaced by τ_α of the supercooled liquid at that temperature, in order to make comparisons between different substances. In this work, for the ethylcyclohexane, τ_α is determined as the reciprocal of the angular frequency of phase angle minimum at that temperature. The results of this analysis are plotted as red stars in Figure 11 and are in good agreement with similar determination using dielectric experiments.

The results from ethylcyclohexane and from toluene, ethylbenzene, indomethacin, and methyl-*m*-toluate show similar trends and the glasses show comparable kinetic stability. All the systems show a sublinear dependence of $t_{\text{transform}}$ on τ_α , as qualitatively anticipated by Wolynes for a supercooled liquid that exhibits spatially heterogeneous dynamics.⁴⁴ The strong connection with τ_α indicates that the mobility of the supercooled liquid controls the rate at which a growth front can move into the stable glass. The deposition rate for ethylcyclohexane is somewhat higher than for the other materials and this partially explains its position at the bottom of the plot. As shown in Figure 9, there is a strong dependence of transformation time on deposition rate. For the substrate temperature of 85 K, the transformation time at 103 K for ethylcyclohexane deposited at 8 nm s⁻¹ is more than half an order of magnitude lower than the transformation time when the deposition rate is 2 nm s⁻¹. Assuming a similar shift at other transformation temperatures, this would bring the ethylcyclohexane data close to the toluene and ethylbenzene curves.

C. Deposition rate dependence

The influence of deposition rate on the kinetic stability of as-deposited glasses was determined by varying the deposition rate by more than four orders of magnitude from 0.002 nm s⁻¹ to 60 nm s⁻¹. We performed these measurements at seven substrate temperatures from 95 K to 60 K, which covers the range from 0.95 T_g to 0.6 T_g . For all experiments, the transformation temperature $T_{\text{transform}}$ was 103 K, the films were ca. 400 nm thick, and the thermal oscillation was 20 Hz.

Figure 8 shows the transformation behavior of as-deposited glasses of ethylcyclohexane deposited at substrate temperatures of 65 K and 85 K at different deposition rates. For each curve, we determine a transformation time marking the end of the transformation into the supercooled liquid. The construction for determination of the transformation time is shown. For substrate temperature of 65 K, we observe that the transformation time lengthens about a factor of 200 as the deposition rate is lowered. At the lowest deposition rate, we observe a long time tail that creates some ambiguity about the determination of $t_{\text{transform}}$, but this ambiguity does not affect our later analysis. For example, in the 0.002 nm s⁻¹ data, the fast process gives $t_{\text{transform}} = 2.4$ h and the long tail yields 15 h. This difference is less than an order of magnitude which is within the scatter of Figure 9. Thus, the decision to use the short or long transformation time does not significantly affect the discussion. The experiments presented here explore the temperature region below 0.8 T_g for the

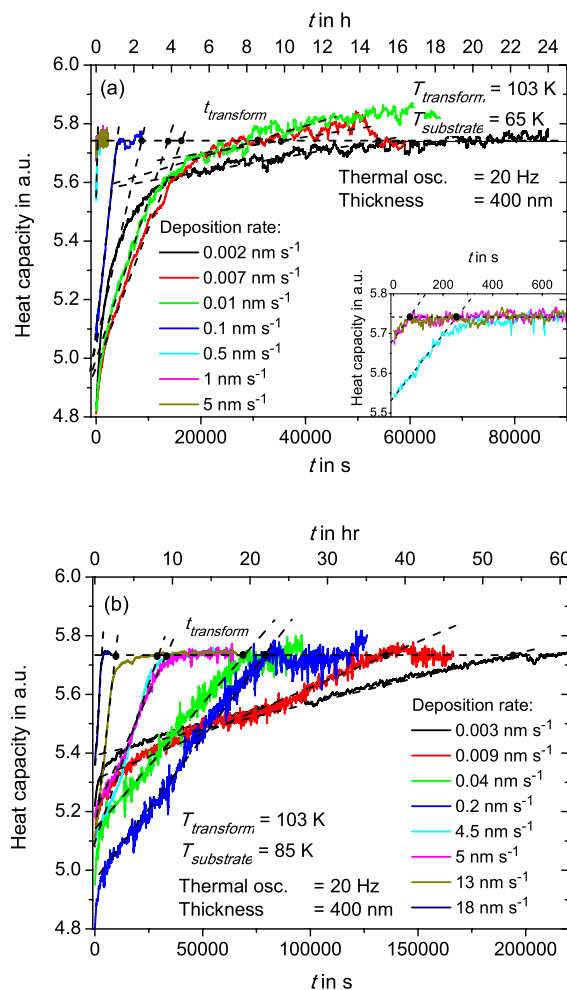


FIG. 8. Isothermal transformation kinetics at transformation temperature 103 K of as-deposited glasses of ethylcyclohexane into supercooled liquid, for different deposition rates. The samples were deposited at substrate temperature (a) 65 K and (b) 85 K. The curves for all substrate temperatures are shown in the supplementary material.⁴⁸

first time in a systematic manner regarding the effect of the deposition rate on kinetic stability. For substrate temperatures between T_g and 0.8 T_g , the transformations at 103 K are fairly linear with time, supporting a growth front moving at constant speed from the free surface towards the substrate, Figure 8(b). The nonlinear shape for the transformations of the slowest deposited samples at lower substrate temperatures indicates a more complex transformation mechanism, which is currently unknown. The identification of this mechanism is an important target for future research. It may require a better knowledge about co-deposited impurities, which may enrich at the transformation front and slow down transformation.

The transformation times as a function of deposition rate (top axis) are shown in Figure 9 for seven different substrate temperatures. Unfortunately, transformation times below 100 s are not reliable due to the time required to equilibrate the sensor temperature and the lock-in signal. Thus, we do not report any transformation times below 100 s in Figure 9. At each substrate temperature, lower deposition rates result in higher kinetic stability, presumably because the time available for a molecule to sample different configurations increases.

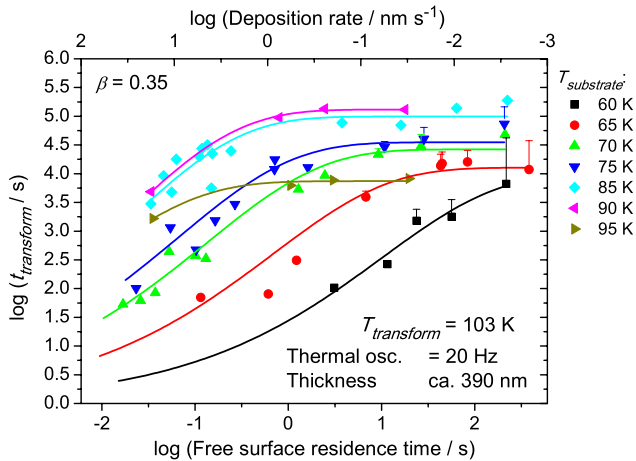


FIG. 9. The isothermal transformation time as a function of free surface residence time, which is the time needed to deposit one monolayer of ethylcyclohexane. The free surface residence time is calculated from the deposition rate which is given on the top axis. The positive error bars for the longest free surface residence times include the two possible transformation times, as indicated in Figure 8(a). Otherwise, the error for transformation times is about twice the symbol size. The transformation times below 100 s are not accessible for instrumental reasons.

For deposition temperatures between 65 K and 95 K, a clear stability plateau is observed at the lowest deposition rates.

To provide a molecular interpretation of the results, the free surface residence time is defined (and plotted as the bottom axis). In the absence of other information, we suppose that the mobile portion of the surface involves only the top monolayer. In this case, the time needed to deposit one monolayer is the time that the average molecule is part of the mobile layer. We therefore calculate the free surface residence time by dividing the thickness of one monolayer of ethylcyclohexane (~ 0.6 nm) by the deposition rate in units of nm s^{-1} .

For each substrate temperature, the data in Figure 9 were fit with a stretched exponential function of $\log(t_{\text{transform}})$ as function of free surface residence time

$$\log(t_{\text{transform}}) = \log(t_{\text{transform}})_{t \rightarrow \infty} \cdot [1 - \exp(-(t/\tau_{KWW})^\beta)]. \quad (3)$$

In this equation, $\log(t_{\text{transform}})_{t \rightarrow \infty}$ represents the kinetic stability of the glass in the limit of slow deposition, τ_{KWW} is the time constant, t is the free surface residence time, and β is the stretching exponent with $0 < \beta \leq 1$. For the fits shown in Figure 9, the parameter β is fixed to be 0.35, which is the fit value for the data at substrate temperature 65 K, in order to reduce the number of fit parameters. If β is allowed to vary during the fit, the values obtained are between 0.4 and 0.3.

The parameters obtained by fitting Eq. (3) to the data in Figure 9 are shown in Figure 10. The most surprising feature of these results is that the limiting kinetic stability of ethylcyclohexane glasses decreases with substrate temperature below $0.85 T_g$; we discuss this below.

IV. DISCUSSION

We have investigated the properties of vapor-deposited glasses of ethylcyclohexane with AC nanocalorimetry, varying

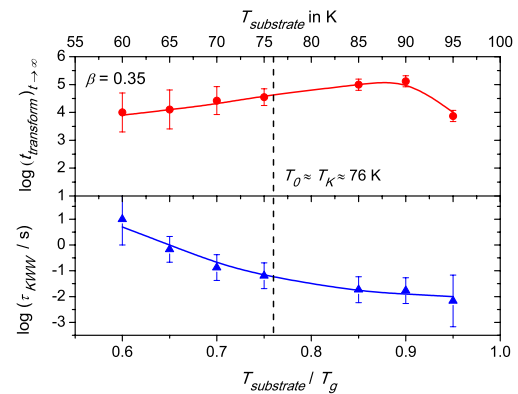


FIG. 10. Fit parameters describing the influence of deposition rate upon kinetic stability for ethylcyclohexane glasses. The upper panel shows the transformation time in the limit of slow deposition, $\log(t_{\text{transform}})_{t \rightarrow \infty}$. The lower panel shows $\log(\tau_{KWW})$ which describes the evolution towards limiting kinetic stability, as function of $T_{\text{substrate}}$, according to Eq. (3) with $\beta = 0.35$ fixed. The lines are guide to the eye.

the transformation temperature, substrate temperature, and the deposition rate across a significant range. The present work provides the first opportunity to investigate how the kinetic stability of the as-deposited glasses depends upon the deposition rate across a wide range (four orders of magnitude) for different substrate temperatures from $0.6 T_g$ to $0.95 T_g$.

We first note that while the data in Figure 9 are more comprehensive than any previous study, they are qualitatively consistent with previous work on other vapor-deposited glasses and with the idea that surface mobility controls the kinetic stability of glasses formed by vapor deposition. For deposition at or above $0.9 T_g$, a deposition rate of 1 nm s^{-1} is adequate to reach the maximum kinetic stability for glasses of ethylcyclohexane. Lowering the deposition rate by

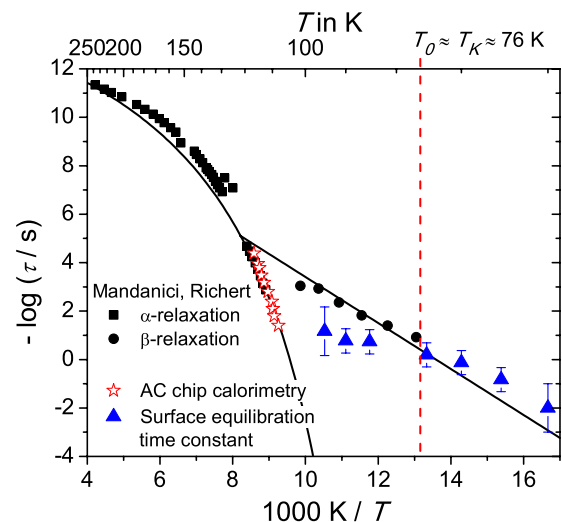


FIG. 11. Characteristic times for liquids and glasses of ethylcyclohexane. The frequency dependence of dynamic glass transition temperatures from AC calorimetry is shown as open red stars. The surface equilibration times $\tau_{\text{surface}} = 10 \tau_{KWW}$ are shown for each substrate temperature as solid blue triangles. Included are solid black squares and circles as dielectric measurements for α - and β -relaxations of ethylcyclohexane, respectively.⁴¹ The determined T_0 (from dielectric) and T_K (from calorimetry) are shown for comparison (dotted red line). The solid curved and straight black lines represent reported fits to the data by the VFT and Arrhenius functions, respectively.

a further one or two orders of magnitude does not further increase the kinetic stability. This would indicate that ~ 1 s is enough time for molecules at the surface to sample a sufficient number of available configurations. These results are qualitatively consistent with the weak dependence of as-deposited glass properties upon deposition rate reported for toluene and ethylbenzene deposited at $0.9 T_g$.^{8,10} However, at lower substrate temperatures, the impact of deposition rate becomes much stronger in the experimental window of deposition rates. For example, for deposition at $0.7 T_g$, the transformation time lengthens by nearly three orders of magnitude with decreasing deposition rate. These results are qualitatively consistent with those previously reported for indomethacin deposited at $0.85 T_g$.² In the present experiments on ethylcyclohexane, ~ 100 s is required at the free surface to sample the configurations relevant for kinetic stability at a substrate temperature of $0.65 T_g$.

A. Surface equilibration times

From the data in Figure 9 and the fits in Figure 10, we can define a surface equilibration time at each deposition temperature. In Figure 9, we note that the experimental data for stability become largely independent of the free surface residence time when this time exceeds τ_{KWW} by a factor of ten. For comparison with other common relaxation processes, we therefore define a surface equilibration time $\tau_{surface} = 10 \cdot \tau_{KWW}$. In Figure 11, we compare $\tau_{surface}$ with the α - and β -relaxation processes for ethylcyclohexane obtained by dielectric relaxation (solid black symbols),⁴¹ and the α process obtained for ethylcyclohexane in this work by AC calorimetry (open red stars).

We observe that the surface equilibration time is within two orders of magnitude of the dielectric β process but does not seem to have the same temperature dependence. Both $\tau_{surface}$ and τ_β have a much weaker temperature dependence than the bulk α -relaxation process. One interpretation of these results would be as follows. Since the β -relaxation process is much more localized than the α -relaxation process, it might be reasonable to assume that τ_β is similar at the free surface and in the bulk. Since we imagine that the surface relaxation process is more cooperative than the β -relaxation process at the surface, it is reasonable to expect that *surface relaxation process* cannot be faster τ_β at the surface. The data in Figure 11 are consistent with this scenario in which the bulk β process sets a “speed limit” for surface relaxation.

In Figure 11, we observe that $\tau_{surface}$ changes smoothly across the range where $T_0 \approx T_K$. Stevenson and Wolynes made a prediction for the surface relaxation time $\tau_{surface} = (\tau_0 \cdot \tau_{bulk})^{0.5}$ based on the random first order transition (RFOT) theory;⁴⁹ here, τ_0 is a constant, ~ 1 ps. If the VFT equation remains correct below the conventional T_g , then the surface relaxation time would diverge at the Vogel temperature T_0 . This is obviously not the case for ethylcyclohexane since even for substrate temperatures below T_0 and T_K , kinetically stable glasses are formed. On the other hand, this finding is in qualitative agreement with the explanation of enhanced surface diffusion by Ngai *et al.*⁵⁰ based on the coupling model. In that approach, $\tau_{surface}$ is identified with τ_β . As we

remarked above, our results are not quantitatively consistent with this prediction.

Near T_g , the surface equilibration time shown in Figure 11 is at least 4 orders of magnitude faster than the structural relaxation time τ_α . This behavior is very similar to the fast crystal growth observed at the surface of low molecular weight glass formers like *o*-terphenyl.⁵¹ Also, the behavior is qualitatively similar to the data on surface self-diffusion in nifedipine and indomethacin, where the difference between surface and bulk diffusion coefficients at T_g is about 7 orders of magnitude.²⁴ It would be necessary to perform all these experiments on a single system in order to understand the quantitative relationship between these observables.

B. Equilibration towards what state?

While we described a surface equilibration time in the discussion above, there is some ambiguity about the nature of the state formed by vapor deposition in the limit of low deposition rates. The most puzzling observation in these experiments is presented in Figure 10(a). Note that the $\log(t_{transform})_{t \rightarrow \infty}$ increases with decreasing substrate temperature from T_g to $0.85 T_g$. This is consistent with the idea that the sample equilibrates into the equilibrium supercooled liquid; as a supercooled liquid equilibrates to lower temperatures, it moves lower in the potential energy landscape into regions with higher activation barriers, which then increases transformation time. However, below $0.85 T_g$, $\log(t_{transform})_{t \rightarrow \infty}$ decreases with decreasing temperature. This behavior would be unexpected if the state reached in the limit of slow deposition were the equilibrium supercooled liquid. Another possibility is that deposition at very low rates at temperatures below $T_0 \approx T_K$ produces an “ideal glass,” i.e., an amorphous system at the bottom of the potential energy landscape (excluding crystalline states). In this case, we would expect $\log(t_{transform})_{t \rightarrow \infty}$ to become independent of substrate temperature below $T_0 \approx T_K$, since all such depositions would produce essentially the same amorphous structure. This scenario does not seem consistent with the data in Figure 10(a) indicating that $\log(t_{transform})_{t \rightarrow \infty}$ decreases by an order of magnitude as the substrate temperature decreases.

One possible interpretation of these data is suggested by the recent work of Dalal *et al.*⁵² For indomethacin, these authors combine results from a number of experiments to show that deposition between 0.90 and $0.97 T_g$ produces glasses whose properties are independent of deposition rate and match the density and modulus expected for the equilibrium supercooled liquid at these temperatures. However, these glasses are anisotropic as indicated by optical birefringence and wide angle x-ray scattering. This last observation excludes the formation of the equilibrium supercooled liquid. One possibility is that the product of the deposition is a (unknown) liquid crystal phase, lower in free energy than the supercooled liquid. More likely is the possibility that slow deposition produces a system that is equilibrated with respect to surface motion but that the system is higher in free energy than the supercooled liquid. While this idea does not explain why $\log(t_{transform})_{t \rightarrow \infty}$ decreases with decreasing substrate temperature below $0.85 T_g$, it does allow this possibility.

Since the lowest deposition rates are most important here, the problem of water co-deposition cannot be neglected. As we discussed above, at the very lowest deposition rate, there is a possibility of co-deposition of up to 10% water. Water or other co-deposited molecules may disturb the packing of the stable glass and this needs further investigation. However, we observe that $T_{g,dyn}$, as indicated by the phase angle minimum in Figure 4(b), does not change between the first heating (the as-deposited glass) and second heating (the ordinary liquid cooled glass) and is consistent across all deposition temperatures and rates. $T_{g,dyn}$ should be sensitive to significant levels of contaminants in the film that do not have a 110 K structural relaxation time that is very similar to that of ethylcyclohexane. The first and second heatings, having the same minimum in the phase angle, suggest that any contaminants, like water that are molecularly dispersed in the as-deposited film but would likely phase separate after transformation, are not present in significant amounts. Films deposited at lower substrate temperatures and slower rates would be expected to incorporate more contaminants than those deposited at higher substrate temperatures and faster rates. The consistency of $T_{g,dyn}$ across deposition conditions suggests that in general the level of contaminants is low. This observation argues against the presence of molecularly dispersed water in the as-deposited films.

C. Role of fragility in stable glass formation

Ethylcyclohexane, with a kinetic fragility m of 56.5, is near the strong limit of organic glass formers. It has the same m value as glycerol, which is often described as the least fragile organic liquid. Some authors have suggested that fragility might be a controlling factor in the ability to form kinetically stable glasses by vapor deposition, where these materials can only be made from highly fragile liquids.^{32–35} Indeed, it has been suggested that ethylcyclohexane does not form high density, high kinetically stable glasses.^{32,33}

The results in Figures 5 and 6 definitively show that one of the least fragile organic liquids can form glasses of high kinetic stability and extend the range of m values considered in a recent publication.³⁶ Note that methyl- m -toluate (also shown in Figure 6) has an m value of 60 and that glasses of high kinetic stability have been reported with m values up to 147.⁶ While one might get the impression from Figure 6 that ethylcyclohexane is the least kinetically stable of the systems shown that is only because of the deposition rate (8 nm s^{-1}) used to acquire the data in this figure. From Figure 9, we can see that depositing ethylcyclohexane at lower deposition rates increases the transformation time up to values similar to those reported for indomethacin.

V. CONCLUSIONS

Ethylcyclohexane, a strong glass former with kinetic fragility $m = 56.5$, forms kinetically stable glasses by vapor deposition at a wide range of substrate temperature from 0.6 to $0.95 T_g$. The kinetic stability, judged from the isothermal transformation time of the as-deposited glasses, depends on

substrate temperature and deposition rate. An increasing free surface residence time, produced by lowering the deposition rate, is required to form kinetically stable glasses at decreasing substrate temperatures. The surface equilibration time shows an Arrhenius temperature dependence from T_g down to $0.6 T_g$ and is within two orders of magnitude of the β -relaxation time. The obtained data are in agreement with the hypothesis that kinetically stable glasses form as a result of surface mobility. The dramatic slowing down of the main relaxation process near T_g does not preclude the ability to form kinetically stable glasses and kinetically stable glasses are formed even below $T_0 \approx T_K$. Surprisingly, the glasses formed in the limit of slow deposition at the lowest substrate temperatures are not as kinetically stable as those formed near $0.85 T_g$.

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