

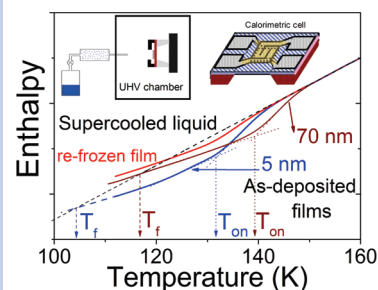
Size Effects and Extraordinary Stability of Ultrathin Vapor Deposited Glassy Films of Toluene

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ABSTRACT We report the first experimental evidence of size effects in the glass transition of thin films of an organic molecule grown from the vapor phase. In as-deposited films grown at 90 K ($0.80T_g$), both the fictive temperature, T_f , and the onset of the glass transition, T_{on} , decrease with thickness. The thinnest layers (~ 4 nm) exhibit the highest thermodynamic and lowest kinetic stability. Films refrozen at 2000 K/s after being heated to the liquid state during a previous scan demonstrate no size effects. The width of the glass transition for both as-deposited and refrozen films is independent of the film thickness down to 4 nm. Our heat capacity data suggest that ultrathin vapor-deposited glasses transform into liquid by a faster dynamic influenced by the outer film surface.

SECTION Nanoparticles and Nanostructures



In spite of a tremendous amount of work in the past few decades, a clear understanding of glass formation remains elusive and is one of the most important challenges in solid-state physics.^{1–3} In molecular liquids, the translational degrees of freedom of a supercooled liquid become largely frozen at the glass transition temperature. Toluene is a particularly simple glass-forming molecule with a calorimetric glass transition temperature, T_g , of 117.5 K^{4,5} and a fragility index $m = 105$.⁶ Experimental studies of confinement effects of small molecules in nanopores^{7–10} may shed light on the nature of the glass transition and calorimetric measurements of T_g . However, a unique interpretation of the results of such studies is difficult since the measured onset temperatures of the glass transition decrease, increase, or remain equal to that of the bulk depending on the particular system and the interaction of the fluid with the solid.¹⁰

Supported ultrathin films represent a particularly useful configuration for analyzing size effects, although calorimetric studies in glass-forming liquids with subambient glass transition temperatures are experimentally challenging. Only recently have developments in nanocalorimetry been successfully applied to glass-forming liquids.^{11,12} Nanocalorimetry has already proven its potentiality to analyze the glass transition of ultrathin polymer films. Recent data by Allen et al.^{13,14} and Schick et al.¹⁵ suggest the absence of size effects in thin supported films of polystyrene and poly(methyl methacrylate), contrary to observations made by many authors using different techniques.^{16–18} Fakhraei and Forrest¹⁸ analyzed the influence of the cooling rate on the glass transition temperature of thin supported polystyrene films and concluded that, in fact, previous measurements were heavily influenced by the thermal history of the sample. Only ultrathin films subjected to slow cooling rates (below 130 K/min)

showed a clear reduction of T_g with decreasing thickness. Also, the influence of the measurement probe frequency on the dynamics of the glass transition for ultrathin films is still under debate.^{18–20}

Of significance to the present work is the recent finding that bulk vapor-deposited glasses possess an extraordinary thermodynamic and kinetic stability, inaccessible by simple annealing procedures of glasses conventionally cooled from the liquid.^{21–24} Such increased stability is linked to both the growth rate and the deposition temperature, T_{dep} , since it results from the increased molecular mobility at the glass surface during deposition.²⁴ Those results have now been extended to smaller molecules such as toluene¹¹ and ethylbenzene²³ for which vapor deposition at temperatures between $0.80T_g$ and $0.85T_g$ produces glassy films with a smaller molar volume or smaller configurational enthalpy with respect to glasses conventionally cooled from the liquid.

In this letter, we report for the first time a direct thermodynamic confirmation of the dimensionality effect on ultrathin glassy films of a simple organic liquid, toluene, grown by physical vapor deposition (PVD). Our in situ heat capacity data, obtained during upscans on films down to a thickness of 4 nm, enable an exhaustive analysis of the influence of confinement on the following key parameters: the onset of the glass transition temperature, the enthalpy of the glass and liquid, and the limiting fictive temperature.

Figure 1 shows representative curves of the heat capacity of AD (Figure 1a) and FC (Figure 1b) samples of different thicknesses. AD refers to as-deposited films from the vapor,

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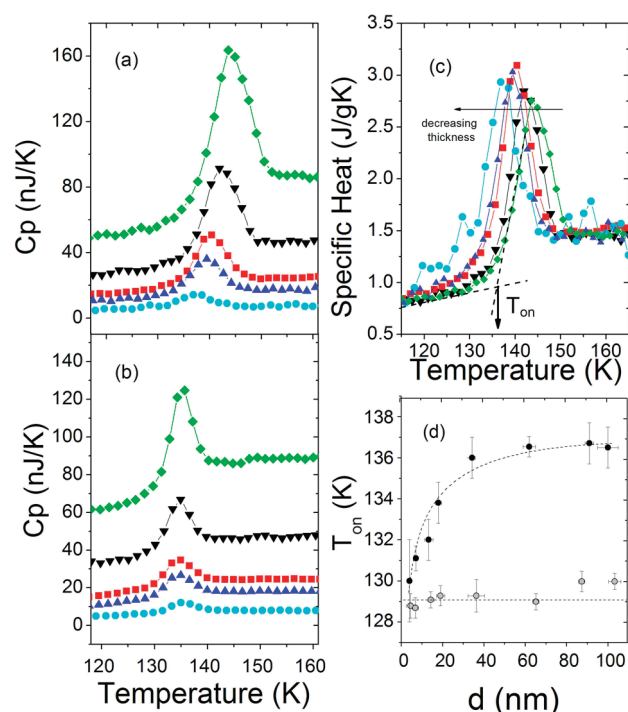


Figure 1. Heat capacity curves for different representative thicknesses (circle: 4 ± 1 nm; up triangle: 13 ± 2 nm; square: 18 ± 1.5 nm; down triangle: 34 ± 1.5 nm; rhombus: 62 ± 3 nm) as a function of temperature. (a) AD (as-deposited) layers (every upscan is a single scan just after growth of the layer). (b) FC (refrozen) samples (every curve is the result of averaging 50 consecutive scans). (c) Specific heat of representative AD samples of various thicknesses. (d) Onset of the glass transition temperature for the two sets of samples, FC (gray circles) and AD (black circles), versus thickness. The lines are guides to the eye.

and FC refers to samples refrozen at 2000 K/s from the liquid (fast-cooled). The mass of the films is determined assuming that the specific heat and the density of the supercooled liquid are identical for all samples and equal to the normal liquid, i.e., $C_p = 1.47013 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$ at 160 K.^{4,5,25} As the deposition area is well-known, the nominal thickness of every sample can be inferred. The onset temperature, T_{on} , is evaluated by extrapolating the heat capacity of the glass and the slope of the peak as shown in Figure 1c. The evolution of the onset temperature with thickness for FC and AD samples is represented in Figure 1d. Every point is the average of three/four independent measurements on equivalent thickness samples. The error bars correspond to the standard deviation. The high value of the onset temperature for the thickest FC films, $T_{on} = 130 \pm 0.5$ K, compared with the bulk value of 117.5 K obtained by differential scanning calorimetry⁵ at 10 K/min, is related to the used high heating rates inherent to the nanocalorimetric technique. In addition, the enhanced kinetic stability of vapor-deposited glasses (the AD films) shifts T_{on} even higher to a value of 137 ± 1 K. The large heat capacity overshoot of AD glasses compared to FC of identical thickness suggest a higher thermodynamic stability of vapor-deposited glasses. While in AD layers the onset temperature decreases with thickness (Figure 1d), in FC samples T_{on} remains approximately constant.

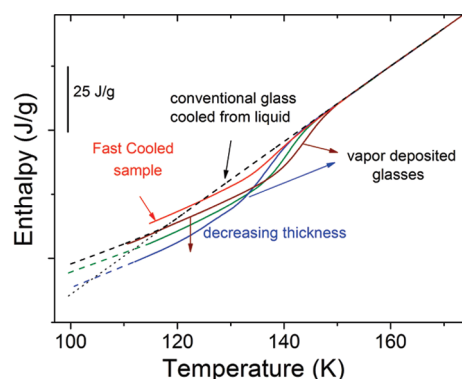


Figure 2. Enthalpy versus temperature for FC (red line) and several AD layers of different thicknesses (brown $d = 91 \pm 3$ nm; green $d = 13 \pm 2$ nm; blue, $d = 4 \pm 1$ nm). The dashed line is constructed by integration of the heat capacity data from Yamamuro et al.,⁴ which corresponds to a conventional liquid. The dashed colored lines are linear extrapolations into the supercooled liquid curve to extract the fictive temperature.

The specific heat data for AD layers in Figure 1c show a clear signature of the glass transition down to a few nanometers. The overshoot of the specific heat in the thinnest AD films is slightly enhanced with respect to thicker ones grown under exactly the same conditions, and the width of the transition remains approximately constant.

The glassy character of the films was demonstrated by extending the calorimetric measurements to above the melting point of the crystalline phase, $T_m = 178$ K.²⁶ The absence of any melting endotherm is a clear indication that both films grown directly from the vapor at 90 K or refrozen from the liquid are disordered. As the energy sensitivity of the nanocalorimetric technique is on the order of 15 nJ in a single scan, we estimate that the crystalline content, if any, must be lower than 5%, in the thinnest films. Our resolution increases with the mass, and the thickest films are glassy within 99%.

The specific enthalpy, evaluated by integrating the specific heat curves after normalizing by the sample mass, is summarized in Figure 2 for several representative samples. The solid curves correspond to the enthalpies of FC and AD layers of different thicknesses upon heating through the glass transition region. We also plot the enthalpy (dashed line) resulting from integration of the specific heat data of Yamamuro et al.⁴ for bulk liquid toluene. We use the polynomial $-182.271 + 1.596T - 4.0548 \times 10^{-4}T^2$ to describe the enthalpy of the supercooled liquid. The limiting fictive temperature, T_f , is obtained from the intersection of the extrapolated liquid curve into the glass region.

Figure 3 is a summary of the T_f values calculated from AD and FC samples as a function of film thickness. T_f reaches 106 ± 2 K for the 4 nm AD films, a value close to the Kauzmann temperature, $T_K = 100$ K.²⁷ Interestingly, for the AD layers, T_f varies as the inverse of the film thickness, obeying an empirical law of the type $T_f(d) = T_f(\infty) + (\Delta/d)$, with $T_f(\infty) = 116.5 \pm 0.5$ K and $\Delta = -43 \pm 4$ nm K. On the other hand, for the layers fast-cooled at 2000 K/s from the liquid, T_f remains approximately constant.

We first focus our analysis on the thickest films of this study. The glassy films reached by cooling the liquid at 2000 K/s are thermodynamically less stable (having higher enthalpy of the

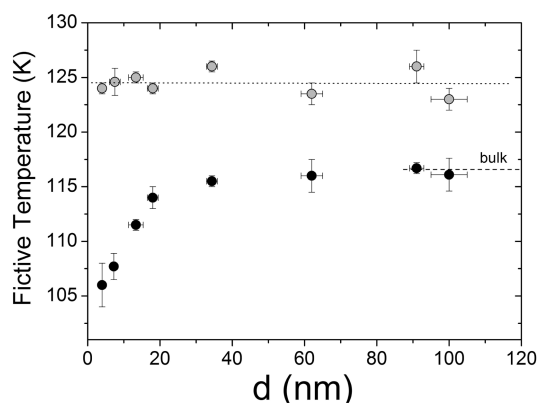


Figure 3. (a) Limiting fictive temperature as a function of thickness for AD (black circles) and FC (gray circles) samples. The dotted line is a guide to the eye.

glass and T_f) as well as kinetically less stable (lower T_{on}) than those deposited from the vapor. Furthermore, the AD layers grown at 90 K in this work are more stable than glasses obtained by cooling the liquid at the slow rate of 5 K/min. Contrary to the current belief that samples deposited from vapor result in unstable glasses, we find that toluene films grown at around $0.8T_g$ have limiting fictive temperatures lower than those cooled from the liquid. This behavior is similar to that reported by Ediger et al. for the larger molecules indomethacin and trisnaphthylbenzene grown at $0.85T_g$.^{21,22,24} The reason may be described in terms of a potential energy landscape as suggested by Kearns et al.²⁴ The loss of kinetic energy upon cooling the liquid is directly linked to the slowing down of the dynamics, thus preventing the molecules from finding equilibrium configurations. The glassy state occurs when the molecules no longer have time to equilibrate and are frozen in local minima of the potential energy landscape. Lower energy in the landscape may be achieved through vapor deposition because surface mobility is enhanced during the deposition process.

Comparing the T_{on} for thick films of both FC and AD samples (Figure 1d), we observe an enhancement in kinetic stability of the thicker AD films, which is related to the more efficient molecular packing attained in vapor-deposited glasses deposited at approximately $0.8T_g$. Aging a thick AD layer at 110 K for several hours did not modify the overshoot peak of the heat capacity nor the onset temperature. The absence of aging effects suggests the AD layer has not progressed further down into the potential energy landscape, implying that the molecular arrangement is already in lower minima than the conventional liquid. That is, the film is already in a dense state, free of voids, and aging does not lead to further densification. This is in agreement with results found for ethylbenzene, in which films obtained by vapor deposition at $0.85T_g$ were denser than films obtained from the liquid.²³ Our data on thick (~ 100 nm) toluene films also demonstrate the presence of a deposition temperature for which T_{on} is maximum and T_f is minimum (unpublished results). As T_{dep} is lowered from 117 to 90 K, the fictive temperature slightly decreases and the onset temperature increases, indicating a higher stability at 90 K, which by

comparison to previous work on other molecules,^{21–23} can be related to a better packing density of the more stable layers.

Several features in our experimental data deserve special attention. First, the presence of large overshoots and narrow peaks in the heat capacity curves of the thinnest AD layers is different from previous calorimetric traces of ultrathin films of polystyrene^{13,28} and confined toluene.²⁵ In those reports, as the thickness decreases, the height of the peak drops, and the full width at half-maximum broadens. This behavior may be linked to both an increased stability of the ultrathin films and the existence of a spatially inhomogeneous surface-initiated mechanism governing the glass transition, as proposed by Swallen et al.²⁹ The expected narrowing of the glass transition region for the thinnest films in this mechanism may be obscured by the temperature broadening of our calorimetric signal.

Second, Figure 2 highlights another remarkable feature arising from the low dimensionality of the stable AD films: the crossover of the enthalpy curves for samples of different thickness. The thickest layers exhibit both a higher glass transition onset temperature and a higher enthalpy in comparison with thinner films. The glass transformation to supercooled liquid in the ultrathin films is advanced with respect to the thick films, and it occurs at a temperature close to that of the fast cooled samples. We obtain an unprecedented simultaneous reduction of T_f and T_{on} with decreasing thickness, which merits further discussion. Since the low fictive temperature of a thick vapor-deposited glass is an indication of its high thermodynamic stability, the lower T_f of the thinnest films is consistent with a scenario in which the molecules lying in the first few nanometers from the surface are positioned in the most energetically favorable positions in the energy landscape. Subsequently, these molecules are buried by other molecules during growth. We speculate that molecules located below the first few nanometers of the surface occupy positions still more favorable than the normal liquid but in a higher energy configuration than the ones at the outer surface. Within this view and even though the molecular packing is still very efficient for the thinnest layers, we attribute their T_{on} reduction to the presence of a distinct outer layer with a faster relaxation dynamic relative to that of the bulk. The variation of 7 K of the onset temperature with thickness (Figure 1d) represents a 100-fold reduction of the relaxation time for the surface layer compared to a thick sample, based on previous data obtained at very fast heating rates.¹² Therefore, the thinnest films, which are indeed more stable (lower T_f), also exhibit a lower T_{on} due to the increased mobility of the surface layer. We use $\Delta T = T_{on} - T_f$ as a qualitative indicator of the stability of the films upon heating. FC layers show a constant value of $\Delta T \sim 7$ K, thick AD films have $\Delta T \sim 21$ K, and thin AD layers have $\Delta T \sim 24$ K. The increased surface-to-volume ratio in the thinner films should result in a larger contribution from the near surface region with enhanced dynamics. Therefore, the thinnest films exhibit the largest variation of the onset temperature. Our calorimetric measurements on ultrathin as-deposited toluene layers reinforce previous observations that the glass transition at the outer surface is depressed with respect to the inner material due to enhanced molecular mobility at the free surface.^{1,3,17}

An exceptional observation in the present work is that, in refrozen samples (FC), the glass transition is independent of thickness. On the other hand, in ultrathin as-deposited toluene glasses (AD), T_f and T_g do vary with thickness. The data of Figures 1–3 support recent findings for polystyrene ultrathin films, for which samples obtained at fast cooling rates showed no T_g depression, while those prepared at slow cooling rates (below 130 K/min) exhibited a strong decrease of T_g with thickness.¹⁸ In this sense, our AD layers may behave similarly to samples that are cooled from the liquid at extremely slow rates.

In conclusion, we have investigated the thickness dependence of toluene thin films grown directly from the vapor or fast cooled from the supercooled liquid. We have demonstrated that the fictive temperature and the onset temperature of the thinnest vapor deposited films are significantly reduced compared to the bulk. In contrast, no variation is observed in samples refrozen at 2000 K/s from the liquid. Our experiments on as-deposited films from the vapor demonstrate an enhanced overshoot of the jump in heat capacity and no broadening of the transition as the thickness decreases. This work strongly suggests enhanced surface mobility and increased stability with respect to the bulk for the vapor deposited ultrathin films.

Thin toluene films were grown by evaporation onto a SiN_x membrane-based calorimetric chip inside an ultrahigh vacuum chamber. Commercial toluene, (purity $\geq 99.9\%$) was purchased from Sigma-Aldrich and used as received without further purification. The liquid was placed in a stainless steel or Pyrex container followed by several freeze–pump–thaw cycles to remove dissolved gases. The liquid was then evaporated into a prechamber at high vacuum and injected into the main chamber with a microcapillary located a few millimeters away from the sample surface. By using a microfabricated shadow mask, glassy films were selectively grown on the active area ($\sim 1 \text{ mm}^2$) of the calorimetric cell. Samples of nominal thicknesses ranging from 4 to 100 nm were deposited at 90 K with a fixed growth rate of $0.040 \pm 0.005 \text{ nm/s}$ either on the Pt surface of the metallic heater or directly onto the silicon nitride membrane. The similarity of the measured data on both surfaces confirms that the size effects we observed were independent of the deposition surface. The heat capacity was obtained using the quasi-adiabatic method developed by Allen et al.³⁰ in which millisecond pulses of electrical current heat the sample at a rate of 10^4 – 10^5 K/s .^{11,30,31} The heating rate was maintained at $3.3 \times 10^4 \text{ K/s}$ throughout this study. Two sets of samples of different thickness were analyzed in depth: AD films grown from the vapor at $T_{\text{dep}} = 90 \text{ K}$ and films that were refrozen at 2000 K/s (FC samples) to 90 K after being heated to the supercooled liquid in the previous scan. AD layers of various thicknesses were also subjected to aging at temperatures slightly below the T_g of bulk toluene.^{4,5} Heat capacity data of the AD layers was obtained from single scans. Since consecutive scans of the FC samples resulted in identical heat capacity curves, we average over 50 consecutive curves to obtain a single C_p curve with a reduced noise. The data treatment includes a box averaging of 80 points to improve the signal-to-noise ratio. The temperature step between adjacent points is 1.25 K.

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