

Novel Method to Detect the Volumetric Glass \rightarrow Liquid Transition at High Pressures: Glycerol as a Test Case

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We report a novel method of detecting the glass \rightarrow liquid transition at high pressures, which comprises measuring the relative volume change incurred upon heating glassy samples into the liquid state. We show data on glycerol in the pressure range 0.050–1.00 GPa to demonstrate the viability of the method. The reversible glass \rightarrow liquid transition is observed by means of a kink in the relative volume change on heating the sample isobarically, which is attributed to the glass \rightarrow liquid transition temperature T_g . This kink can only be observed in the second and subsequent heating cycles since it is superposed by a compaction in the first heating cycle. The isobaric thermal expansivity β , which is closely related to the first derivative of this curve, shows the features expected for a glass \rightarrow liquid transition, including a sharp rise of $\beta(\text{glass})$ in a narrow temperature interval to $\beta(\text{viscous liquid})$ and an accompanying overshoot effect. Both T_g and the size of the overshoot effect vary in accordance with theory upon changing the ratio of cooling to heating rates. From the shape of this curve the onset, inflection, overshoot peak, and endpoint of the glass \rightarrow liquid transition can be extracted, which can be employed to calculate the reduced glass transition width as a measure for the fragility of the liquid. Comparison with literature data allows quantifying the accuracy of the liquid's thermal expansivity β to be at least $\pm 10\%$, while the error in β is significantly larger for the expansivity of the glassy state. The reproducibility of the glass \rightarrow liquid transition temperature T_g is better than ± 2 K. Our glycerol data confirms literature studies showing a nonlinear increase of T_g with increasing pressure (~ 35 K/GPa on average), which is accompanied by an increase in fragility.

1. Introduction

The glass \rightarrow liquid transition is of fundamental importance not only for understanding material properties, e.g., in polymers, but is also a key concept inherent to some theories aimed at understanding the anomalies in liquid water,¹ e.g., the second critical point hypothesis² or the singularity-free hypothesis.³ These theories are based on the assumption that two distinct amorphous states, namely low density amorphous ice (LDA) at pressures $p < 0.2$ GPa and high-density amorphous ice (HDA) at pressures $p > 0.2$ GPa, both experience a glass \rightarrow liquid transition upon isobaric heating. This assumption is, however, debated in the recent literature: the view that LDA at 1 bar behaves crystal-like^{4–7} and does not show a glass \rightarrow liquid transition is diametric to the view that LDA experiences a glass \rightarrow liquid transition at a temperature of ~ 136 K.^{8–15} It has also been questioned if HDA is indeed a genuinely amorphous state or rather a microcrystalline state resulting from the collapse of the hexagonal ice lattice.¹⁶ An additional complication in studying the glass \rightarrow liquid transition in amorphous ice is crystallization, which interferes with the glass \rightarrow liquid transition, and so it has been argued that crystallization precedes a possible glass \rightarrow liquid transition.^{17–19} All these studies have been carried out at 1 bar. At elevated pressures there is hardly any literature available related to water's glass \rightarrow liquid transition. Neither for bulk HDA nor for LDA a glass \rightarrow liquid

transition has been observed so far at high pressures.²⁰ For emulsified HDA it has been suggested to be around 0.4 GPa and 160 K from thermal effects on decompression²¹ or, in conflict with this, at < 140 K both at 0.4 and 1.0 GPa from dielectric relaxation spectroscopy.²²

In order to resolve these issues a technique to investigate the glass \rightarrow liquid transition at isobaric conditions at high pressures is required. The most widely employed methods to study the glass \rightarrow liquid transition at 1 bar are differential scanning calorimetry (DSC), viscosimetry and dilatometry.^{23,24} High-pressure/low-temperature calorimeters are very scarce, and commercial systems are typically limited by maximum pressures of about 0.02 GPa. They are not suitable to scrutinize a possible glass \rightarrow liquid transition in HDA, since HDA is unstable with respect to LDA at $p < 0.2$ GPa.²⁵ Viscosimetry at high pressures is feasible in the measuring range of 10^{-3} – 10^7 Poise using a diamond anvil cell viscosimeter.²⁶ At the glass \rightarrow liquid transition the viscosity is by a common definition 10^{13} Poise, and so an extrapolation of 6 orders of magnitude is required to locate the glass \rightarrow liquid transition using viscosity measurements. Because of these weaknesses we have developed a volumetric method using a material testing machine and a piston-cylinder apparatus, which allows studying the isobaric glass \rightarrow liquid transition at pressures up to 2 GPa and at temperatures down to 77 K. The technique is based on measuring the discontinuity in the thermal expansivity β at the glass \rightarrow liquid transition and, therefore, allows determination of the glass \rightarrow liquid transition temperature T_g , its pressure

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dependence dT_g/dp , and the change in thermal expansivity $\Delta\beta$ at T_g , which is a measure for the fragility of a glass-forming liquid.²⁷ The expansivity “will generally show more pronounced changes at T_g than the heat capacity because the glass expansivity is mainly determined by the anharmonic component of the atomic motions. The behavior of β about T_g , like that of c_p , reflects changes in short-range order that occur when $T > T_g$. Thus, $\Delta\beta$ can show all the variations associated with rate of short-range order breakdown seen for c_p .”²⁸ Observation of $\Delta\beta$ is hence as well suited for inferring a glass \rightarrow liquid transition as observation of Δc_p is. High-pressure differential thermal analysis (DTA) or high-pressure differential scanning calorimetry (DSC) would be suitable tools to provide complementary information regarding the glass \rightarrow liquid transition at high pressures. In the past only a few such systems have been constructed^{29–32} and only a few studies on the glass \rightarrow liquid transition were reported with these techniques.³³ In principle the glass \rightarrow liquid transition can be observed for one-component systems in any of the multidimensional directions in the pressure-temperature-volume space,³⁴ e.g., by observing the change in compressibility or the heat of compression using the volume vs pressure method.^{21,33} It is possible that, as in SiO_2 , the change in compressibility, unlike the change in heat capacity, will be large at T_g for a substance like water.³⁵

It is possible that in amorphous ices crystallization cuts off the glass \rightarrow liquid transition before its endpoint is reached (or even before its onset is observable) also at high pressures — this is subject to further investigation with our method. In order to avoid the complication of crystallization and to have the opportunity to compare our results with literature data we have studied glycerol to benchmark the method. Glycerol is a well-known and good glass-former, which does not easily crystallize. As early as at the turn of the 19th century it was found that its dielectric constant ϵ decreases from ~ 55 to ~ 3 on cooling from 210 to 170 K.³⁶ The specific heat capacity c_p shows a rough doubling in the interval 180–190 K.³⁷ An abrupt doubling of the expansivity β was inferred from a crude dilatometric method.³⁸ Compared to other well-known glass-formers glycerol is a severe test case for our method since it shows a comparatively small change in expansivity at T_g . The most comprehensive study at 1 bar was done by Schulz³⁹ and reviewed by Ubbelohde.⁴⁰ He reported a jump-like change of β , c_p , ϵ and thermal conductivity λ at roughly the same temperature of $T_g \approx 184$ K and 1 bar. Later T_g has been placed at ~ 186 K⁴¹ or ~ 193 K.⁴² The first study of the high-pressure behavior of glycerol was reported by Danforth in 1931 under isothermal conditions.⁴³ Also later most of the studies related to glycerol’s glass liquid transition under pressure have been conducted isothermally.^{26,44–49} In this work we investigate glycerol’s glass \rightarrow liquid transition to the best of our knowledge for the first time isobarically at pressures exceeding 0.020 GPa. When the logarithm of glycerol’s viscosity is plotted versus the reduced temperature (“Angell plot”) it turns out to be of intermediate fragility at 1 bar.⁴⁶ Its fragility increases with increasing pressure and it becomes almost as fragile as the prime example for a fragile liquid (*o*-terphenyl) at a pressure of about 3 GPa (cf. Figure 7 in ref 46). Paluch et al. have noted an increase in fragility (as judged from the steepness index) for pressures up to 1 GPa, whereas it remains essentially constant from 1 to 6 GPa (cf. Figure 4 in ref 48). This would make glycerol one of the few, if not the only one, substances showing an increase in fragility as the pressure increases. By contrast, Reiser and Kasper find that glycerol’s fragility is essentially constant up to 0.7 GPa using dielectric spectroscopy.⁵⁰ T_g

increases nonlinearly with increasing pressure with a slope of about 35 K/GPa (cf. Figure 3 in ref 48) or 50 K/GPa between 0 and 1 GPa (cf. Figure 6 in ref 46) and reaches about 300 K at a pressure of 5 GPa (cf. Figure 6 in ref 26). Such a slope is generally found for polyalcohols like glycerol or D-sorbitol.^{51,52}

2. Experimental Method

Our setup is shown schematically in Figure 1. A ceramic (9) and a Bakelite disc (8) are placed on the steel table (10) of our material testing machine Zwick, model BZ100/TL3S with a positional reproducibility of $\pm 5 \mu\text{m}$ and a spatial resolution of $0.01 \mu\text{m}$. Next, a steel disc (4) and the cylinder of about 1 kg shown in more detail in Figure 1b with a small piston (3) are placed inside an insulated steel pot (6, 7). This cylinder is equipped with two resistance heaters and a Pt-100 temperature sensor, which snugly fit into the holes (15). The pot is filled with liquid nitrogen up to the level indicated in Figure 1a. While the system cools an open cylindrical indium container (200–350 mg indium) is placed at the bottom of the bore (1). A 300.0 mm³ sample of glycerol of a density 1.260 g/cm³, i.e., 378.0 mg, is then pipetted into this container at temperatures below 180 K, which causes immediate vitrification. The role of indium, a very soft and easily deformable metal, is to act as a lubricant reducing piston friction also at temperatures as low as 77 K. The second small piston and the large piston (3) are pushed into the bore; a steel disc (4), a Bakelite disc (8), and a second steel disc (4) are placed on top of the piston (3). The crossbeam is moved downward using a computerized interface (software TestXpert V7.1) at a sample temperature of 77 K and builds up a force of 1000 N, which is kept for a few seconds. Next, the crossbeam moves down slowly at a controlled rate of 20 MPa/min to reach the desired pressure, e.g., 0.050 GPa for some experiments described in the results section. The piston position reached at this time serves as “zero” for both piston displacement and time. This pressure is then kept constant using an algorithm that moves the piston once the time gradient of pressure deviates from zero. Once all liquid nitrogen has evaporated, the whole cylinder including the sample warms up. We directly measure the piston displacement and the temperature—the isobaric expansivity $\Delta\beta$ is inferred from the first derivative of this curve and literature data for the absolute molar volume at high pressures.⁴³ Our current piston-cylinder setup with a bore diameter of 8 mm and our material testing machine calibrated for forces of 200–100 000 N gives us an operating range of 4 MPa–2 GPa, which encompasses the regions of metastability of all known states of amorphous ice.^{53–56}

The thermal expansion β of the apparatus itself amounts to $\sim 3 \times 10^{-4} \text{ K}^{-1}$ at 160 K and $\sim 4 \times 10^{-4} \text{ K}^{-1}$ at 240 K in the whole pressure range studied. The apparatus’ expansivity approximately equals the expansivity of glassy glycerol, but is much smaller than the expansivity of liquid glycerol. It is, therefore, difficult to quote a reliable value for β (glassy glycerol). From the difference of the two large values we estimate the thermal expansivity of glassy glycerol at 100 K to be $< 5 \pm 4 \times 10^{-5} \text{ K}^{-1}$. This is at least an order of magnitude less than β (supercooled liquid glycerol). For comparison the expansivity at 1 bar was measured to be $\sim 9 \times 10^{-5} \text{ K}^{-1}$ in the glassy state (100 K) and $\sim 5 \times 10^{-4} \text{ K}^{-1}$ in the supercooled liquid state (230 K) with an overshoot comparable to the one observed here for the second heating cycle (cf. Figure 16.10 in ref 40 or Abb. 7 in ref 39). Our method is hence well suitable for measuring β (supercooled liquid glycerol) and also for the jump in expansivity $\Delta\beta$ at T_g .

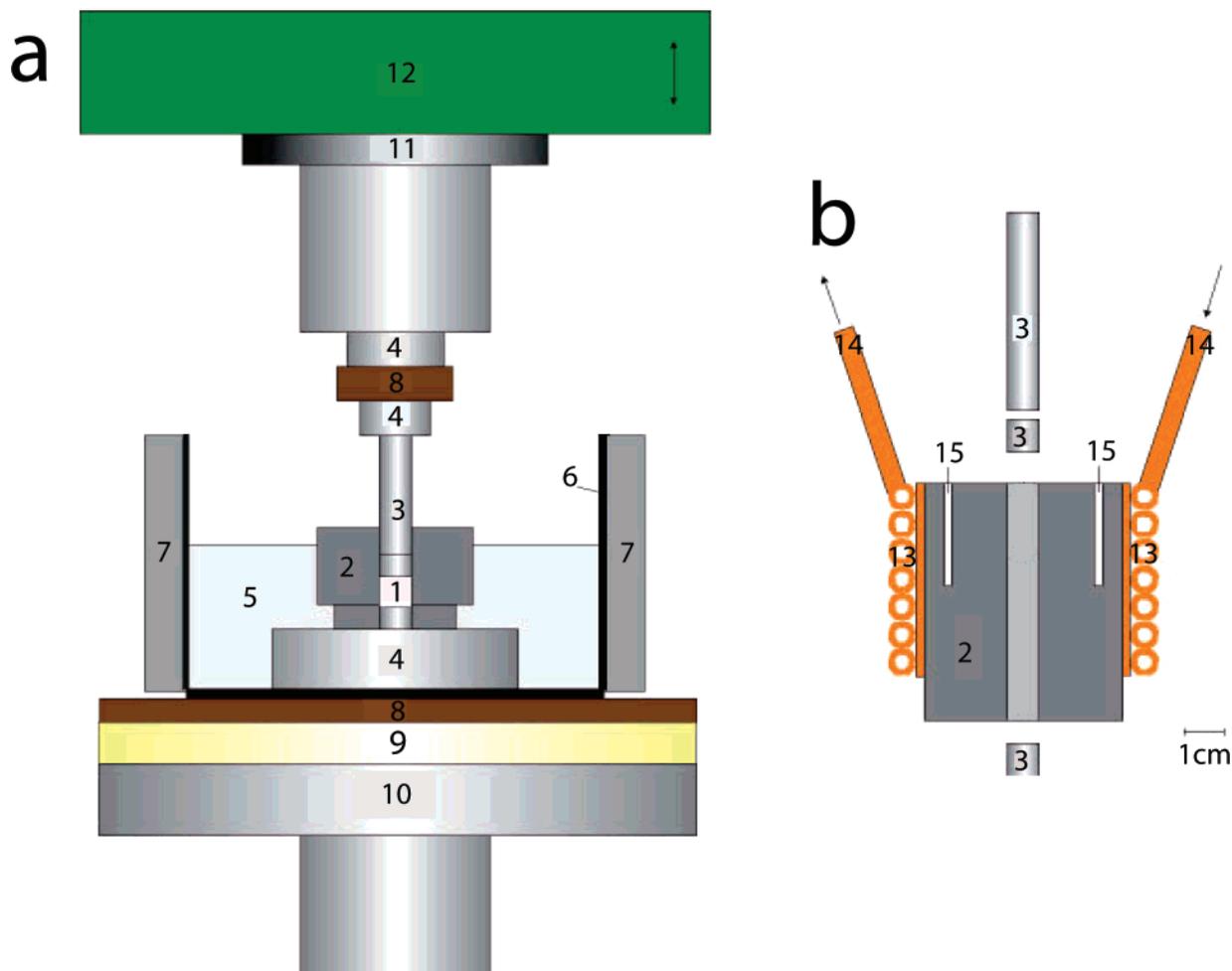


Figure 1. Schematic illustration of our setup. (a) 1, glycerol sample in indium container; 2, cylinder with 8 mm bore; 3, piston; 4, hardened steel disc; 5, liquid nitrogen; 6, stainless steel pot; 7, thermal insulation; 8, Bakelite disc; 9, ceramic disc; 10, immobile steel table; 11, piezoelectric pressure pickup; 12, mobile crossbar. (b) 13, copper loops for liquid nitrogen cooling; 14, connection to liquid nitrogen reservoir and pump; 15, holes for resistive heaters and Pt-100 temperature sensor.

3. Results and Discussion

3.1. Glycerol at 0.050 GPa. 3.1.1. Irreversible First Heating.

In Figure 2 the temperature cycle (panel a), the relative change of volume incurred upon first (panel b) and subsequent heating runs (panel c) as well as all cooling runs (panel d) are shown together with the (uncorrected) thermal expansivity derived from the data (panel e) and the recorded pressure (panel f). For this experiment the heating rate deduced from Figure 2a amounts to ~ 2.5 K/min in the relevant range 160–210 K and is constant to a very good approximation. The average cooling rate is about 10 times as high since liquid nitrogen is poured directly into the pot holding the sample-cylinder. By contrast to the heating rate the cooling rate is not constant over the whole range, but rather increases to a maximum value and then remains constant. For the second, third, and fourth heating cycles in Figure 2, the cooling rate increases while cooling from 210 to 195 K, but remains constant (~ 25 K/min) to a good approximation while cooling from 195 to 160 K. In Figure 2b–d the relative volume change incurred upon performing the temperature cycle seen in Figure 2a is shown. Please note that we directly measure a relative axial piston displacement Δd , which is converted to a relative volume change ΔV simply by multiplying with the bore cross section (50.3 mm^2). These relative volume changes can be converted to absolute volumes since we produce a state of known absolute volume, namely liquid glycerol at 0.050 GPa, which was reported by Danforth.⁴³ It is evident that there is a

significant difference between first heating shown in Figure 2b and subsequent heating cycles shown in Figure 2c. In particular, there is a significant compaction effect, i.e., negative volume change, in the temperature range ~ 155 –185 K in Figure 2b, which is absent in subsequent heating cycles (Figure 2c). Such an increase in density upon heating is unusual and is observed only once (first heating) as an irreversible effect. In the temperature range from 77–150 K (not explored in the experiment shown in Figure 2) and at temperatures > 190 K, an almost linear volume increase, i.e., density decrease, caused by thermal expansion is observed. Please note that the size of this effect experienced upon first heating cycle is not quantitatively reproducible. It depends, e.g., on the rate of pipetting or on the cylinder temperature at the time of pipetting, i.e., the thermomechanical history. We attribute this compaction effect in the first heating cycle, therefore, to microstructural defects (voids, cracks, etc.) resulting from the sample preparation procedure. These defects do not heal at low temperatures ($T < 150$ K), but are being healed once the temperature comes close to what we later attribute to the glass → liquid transition temperature T_g , i.e., once individual molecules are mobile enough to find the (metastable) minimum energy position. For the example shown in Figure 2b the compaction amounts to almost 60 mm^3 . The density of glycerol at 0.050 GPa was determined to be 1.274 g/cm^3 at 348 K and 1.292 g/cm^3 at 303 K.⁴³ On linear extrapolation the density of glycerol is 1.333 g/

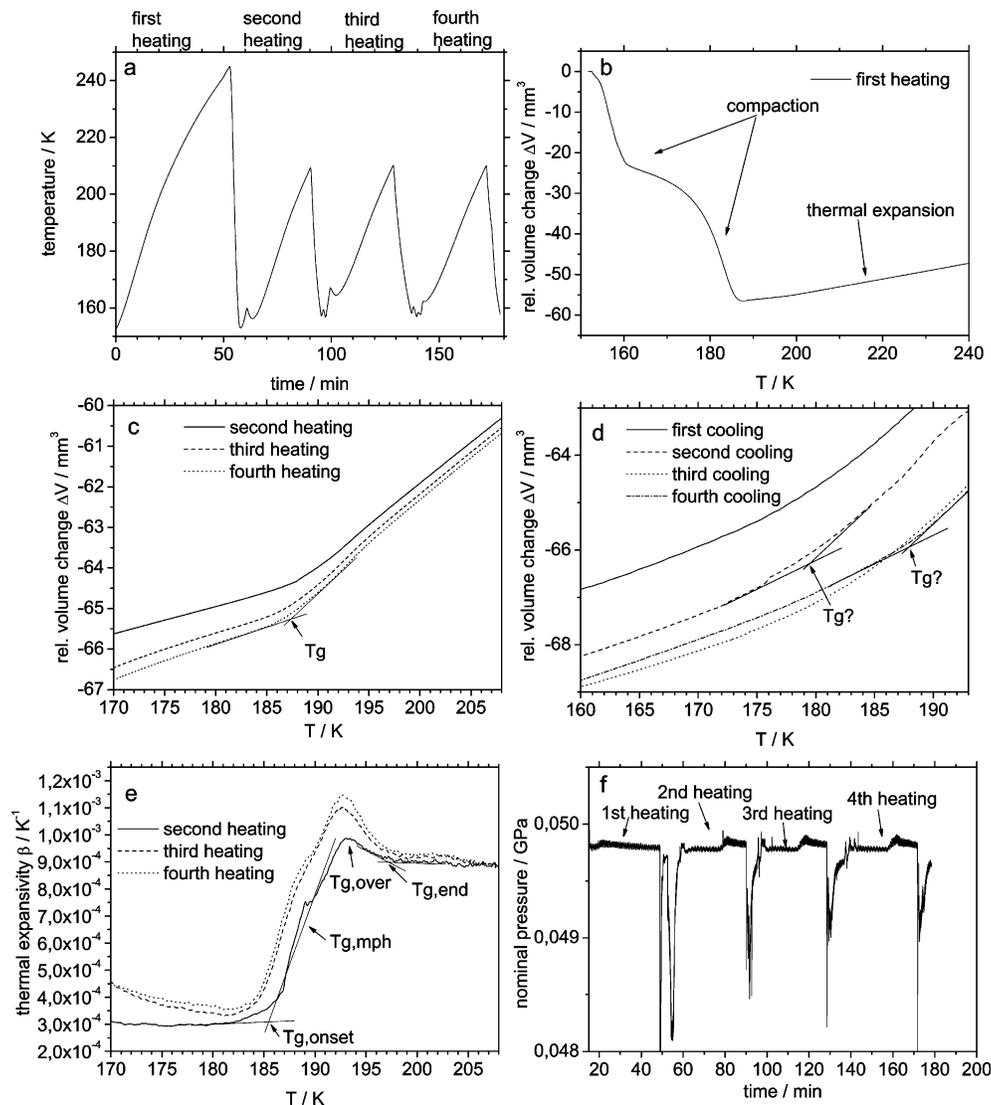


Figure 2. Glycerol's glass \rightarrow liquid transition at 0.050 GPa. (a) Temperature history of the sample and (b) relative volume changes (negative values correspond to densification, positive values correspond to expansion) incurred upon heating the sample for the first time. Curves have been calculated directly from the uniaxial piston displacement by multiplying with the sample cross sectional area without subtracting a background. (c) Relative volume changes incurred upon subsequent heating runs, (d) relative volume changes incurred upon cooling runs, (e) thermal expansivity (not corrected for the apparatus expansivity) calculated as first derivative of data in Figure 2c, together with density data,⁴³ and (f) nominal pressure history of the sample.

cm^3 at 200 K and 0.050 GPa. For 378.0 mg glycerol, this corresponds to an absolute volume of 284.0 mm^3 . The compaction effect, therefore, increases the density by roughly 20% for the example shown. In other experiments we observed somewhat smaller density increases ranging from 5–10% due to different thermal histories. It has been noted by Carruba et al. that even if the effects seen on first heating are not quantitatively reproducible, the effects observed in subsequent heating cycles are reproducible to a high precision,⁵⁷ or in other words: the sample is in a well defined, reproducible state after the first heating cycle, but not before.

3.1.2. Reversible Glass \rightarrow Liquid Transition: Our data shown in Figure 2c confirms this claim. On second heating glycerol never shows a volume change with negative sign (density increase), but rather shows two almost linear regimes of positive volume change separated by a kink at $\sim 188 \text{ K}$. This temperature is reproducible to $\pm 1 \text{ K}$ in the third and fourth (and any subsequent) heating runs. The curves shown in Figure 2c are highly reminiscent of the glass \rightarrow liquid transition textbook examples of volume vs temperature.^{23,24} We, therefore, attribute the kink at $\sim 188 \text{ K}$ to the glass \rightarrow liquid transition temperature

T_g of glycerol at 0.050 GPa at a heating rate of 2.5 K/min and a prior cooling rate of 25 K/min. The temperature of the glass \rightarrow liquid transition (T_g) is determined as the intersection of two tangents according to Figure 4.4 in ref 58. Our assignment of T_g is confirmed by comparison with the values mentioned in the introduction for glycerol at 1 bar ($T_g \approx 180\text{--}190 \text{ K}$)^{38,39,41,42} and using the approximate value of 50 K/GPa⁴⁶ for the pressure dependence of T_g . Upon cooling (cf. Figure 2d) a kink cannot be clearly identified from the data. The kink is blurred and smoothed out over a broader temperature range, and it is ambiguous where to put the two tangents required for determining T_g from the cooling curves. For the fourth cooling run the method of tangents yields $T_g \approx 188 \text{ K}$ in agreement with the heating runs, whereas for the other three cooling runs T_g is found in the range 178–185 K. We conclude, therefore, that cooling runs are not well suited for determining T_g . We believe this is related to the difficulty in maintaining constant pressure for cooling runs (cf. Figure 2f) as well as in establishing a constant cooling rate of the 1 kg cylinder in the entire temperature range of relevance. Nevertheless, after a heating/cooling cycle the relative volume, e.g., at 170 K, is identical within 1 mm^3 to the

relative volume before the heating/ cooling cycle. This demonstrates the reversibility of the isobaric glass \rightarrow liquid transition.

3.1.3 Expansivity and Fragility. In Figure 2e the thermal expansivity $\beta = 1/V \times (dV/dT)_p$ is depicted. This curve has the shape expected for the volumetric glass transition. It shows all the features also evident in typical plots of the calorimetric glass transition including the overshoot typical for heating runs as shown, e.g., in Figure 2 of ref 27: the glass transition onset temperature ($T_{g,onset}$) at 185 K, the midpoint ($T_{g,mp}$) at 189 K, the overshoot peak ($T_{g,over}$) at 193 K and the endpoint ($T_{g,end}$) at 197 K, which can be read from the data with an accuracy of ± 1 K. The glass transition width $\Delta T_g (=T_{g,end} - T_{g,onset})$ amounts to 12 ± 1 K and translates into a reduced glass transition width of 0.065 ($=\Delta T_g/T_{g,onset}$), which is a typical value for a substance of intermediate fragility (cf. ref 27 for the concept of fragility). Figure 2 in ref 59 quotes a value of ~ 0.050 for glycerol at 1 bar, which is reasonably close to our estimate at 0.050 GPa. We note, however, that these values cannot be compared directly since (a) there is a difference in pressure, (b) $T_{g,onset}$ depends on cooling/heating rate, and (c) there is also a cooling rate dependence of the glass transition width.^{60,61} Regarding issue b we determine $T_g \approx 186$ K at 0.050 GPa at a heating rate of ~ 2.5 K/min after prior cooling at ~ 1.0 K/min, i.e., there is a shift by about -2 K in T_g when reducing the cooling rate by a factor of ~ 20 – 30 at the same heating rate and pressure. Such a shift of T_g to lower temperature by decreasing the cooling rate is expected from theory⁶² and can be rationalized in terms of an increasing fictive temperature.⁶⁰ Also the variation in the size of the overshoot matches the textbook expectations for a glass \rightarrow liquid transition when it is observed after cooling at various rates followed by reheating at a single rate^{24,60,63} and provides additional support that we indeed observe a glass \rightarrow liquid transition. According to Blazhnev et al. this temperature dependence (including the overshoot) can be explained in the framework of a microinhomogeneous structure of glycerol first of all by the nucleation process and the freezing-out of the orientational degrees of freedom in the liquid that surrounds nuclei (cf. Figure 1 in ref 64).

3.1.4. Is the Pressure Really Constant? Before proceeding to the pressure dependence we want to show in Figure 2f how the nominal pressure (calculated as applied force divided by bore area) evolves with time in this experiment. It can be seen that the differential algorithm employed to keep the pressure constant results in pressure variations of less than 1×10^{-4} GPa for the whole heating runs, which is typical not only for the experiment shown in Figure 2 at 0.050 GPa, but also for the experiments conducted at 1.00 GPa (not shown). That is, the pressure is constant to better than 0.2% during heating runs at 0.050 GPa and to better than 0.01% during heating at 1.00 GPa. Even in the case of the sudden compaction of about 60 mm^3 shown in Figure 2b the pressure does not drop by more than 0.2%. However, when the system is cooled suddenly by direct contact with liquid nitrogen the pressure drops temporarily by up to 2×10^{-3} GPa (to 96% of the desired pressure in case of 0.050 GPa). That is, while the condition of constant pressure is not fulfilled strictly for the cooling curves in Figure 2d, it is fulfilled to a high degree for the heating curves shown in Figures 2c and 3b so that the notion “isobaric” glass \rightarrow liquid transition seems justified. We emphasize that measurements of isobaric expansivity are thought to be notoriously difficult because of issues with changing pressures. We note, however, that this is typically the case for conventional hydraulic mega- or gigaton presses, but not for our computerized material testing machine

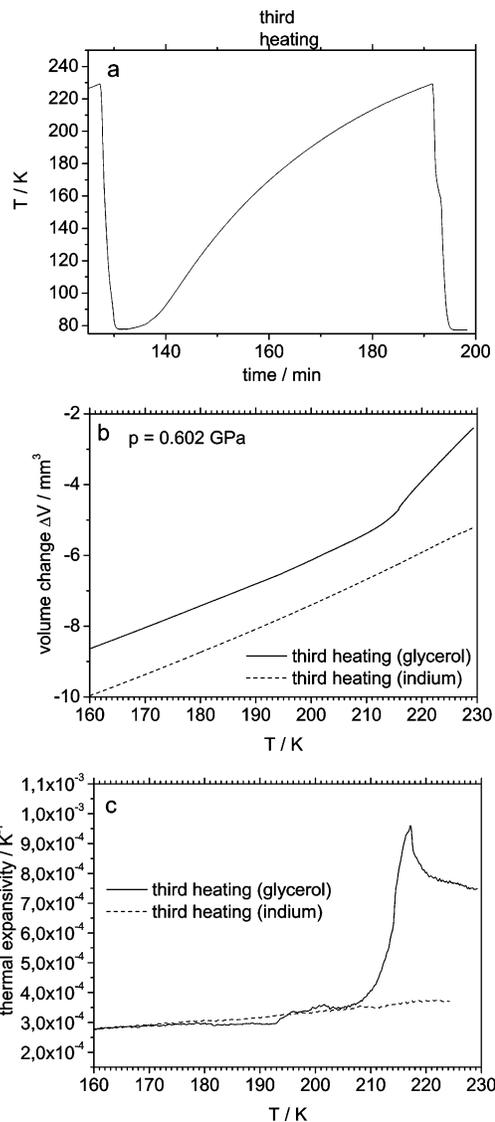


Figure 3. Glycerol’s glass \rightarrow liquid transition at 0.602 GPa. (a) Temperature history of the sample, (b) relative volume changes incurred upon heating together with blind experiment (“indium”), and (c) thermal expansivity together with blind experiment (“indium”).

employing an algorithm to compensate for these pressure instabilities, which is based on the differential change in piston displacement and a proportional-integral-derivative (PID) algorithm, which is a widely used algorithm in control theory to control output variables such as temperature or pressure. We view this automated algorithm of readjusting the pressure as the decisive advantage of our setup. It would not be possible to keep the pressure constant using a manually controlled press rather than an automated material testing machine—these presses typically operate under isochoric conditions. On manually readjusting the pressure, the changes caused by compressing the sample would be superimposed to the changes caused by thermal expansion, and so the glass \rightarrow liquid transition as signalled by the kink in volume change would be blurred.

3.2. Pressure Dependence of Glycerol’s Glass \rightarrow Liquid Transition. **3.2.1. Glycerol at 0.602 GPa.** We now turn to the pressure dependence of the glass \rightarrow liquid transition as measured by our setup. Figure 3a shows the relevant portion of the temperature history for experiments analogous to the experiments in Figure 2, but done at a pressure of 0.602 GPa rather than 0.050 GPa. The heating rate in the range 200–230 K is approximately linear and amounts to 1.6 K/min for the third

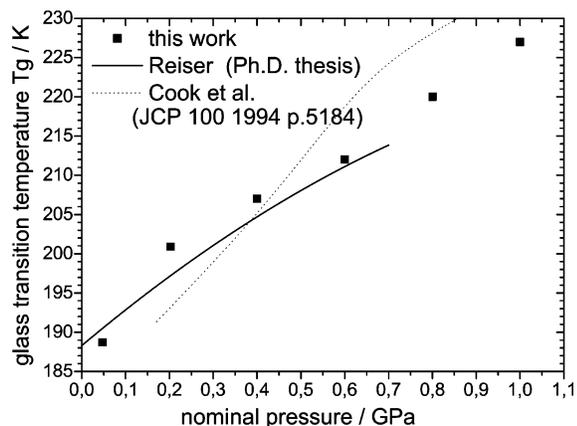


Figure 4. Summary of glass to liquid transition temperatures T_g as a function of pressure together with literature data from refs 65 and 46. Our data refers to fast cooling (25 K/min) and slow heating (1–3 K/min).

heating run (first and second heating runs are not shown). The cooling rate prior to this heating run is, as for Figure 2, ~ 25 K/min. Figure 2b shows the kink in relative volume versus temperature, which we attribute to the glass \rightarrow liquid transition of glycerol, at $T_g \approx 212$ K. This represents a shift of +24 K caused by the pressure increase from 0.050 to 0.602 GPa. In order to demonstrate that the kink is related to glycerol rather than to our apparatus itself, we show the result of a blind experiment without glycerol, which is labeled “indium” (since indium linings are used as a low-temperature lubricant for all experiments). The blind experiment shows an approximately linear volume increase over the whole temperature range and confirms the assignment of the kink to a material property of glycerol. Similarly, the blind experiment does not result in any sudden increase of thermal expansivity in Figure 3c, while glycerol again shows the sudden increase of β in the narrow temperature interval around T_g . $T_{g,onset}$, $T_{g,mph}$, $T_{g,over}$, and $T_{g,end}$ are determined to be 211, 214, 217, and 220 K, respectively from Figure 3c. This results in a glass transition width of about 9 ± 1 K and a reduced glass transition width of about 0.043. That is, on comparing these data with the data collected at 0.050 GPa a decrease of the width of the glass transition by about 3 K, and a decrease of the reduced glass transition width to about 2/3 is evident. This implies an increasing fragility of glycerol with increasing pressure. Such an increase in fragility with increasing pressure is unusual for liquids such as Van-der-Waals liquids, but expected for hydrogen-bonded systems. In the case of glycerol this increase of fragility in the pressure range up to 1 GPa has also been reported experimentally.^{46,48}

3.2.2. T_g and Fragility as a Function of Pressure. The T_g values obtained from Figures 2c and 3b and additional ones determined in the same manner at other pressures are plotted in Figure 4 together with literature data.^{46,65} It is fair to say that our T_g data agree qualitatively with the literature. For the change of T_g with pressure our slope of $dT_g/dp \approx 33$ K/GPa is closer to the slope of 30 K/GPa reported at the high-pressure end by Reiser⁶⁵ than to the slope of ~ 50 K/GPa reported by Cook et al. from extrapolated viscosimeter data.⁴⁶ A summary on all reduced glass transition width data sets collected at 0.050 and 0.602 GPa together with data collected at four other pressures in the range up to 1.00 GPa is shown in Figure 5. This plot confirms the trend of decreasing glass transition widths as the pressure increases. We emphasize that all data correspond to cooling rates of ~ 25 K/min and heating rates in the range 1.5–3.0 K/min. Other data collected after prior cooling at low rates of, e.g., 1 K/min are not included in the plot, since the

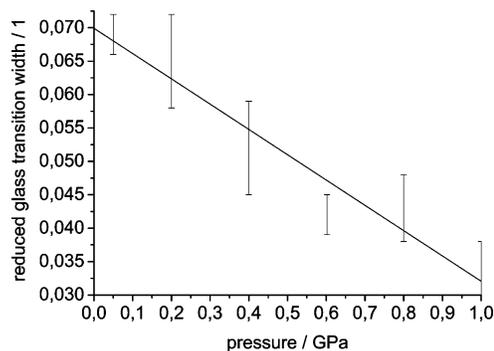


Figure 5. Summary of reduced glass transition widths $(T_{g,end} - T_{g,onset})/T_{g,onset}$ as a function of pressure.

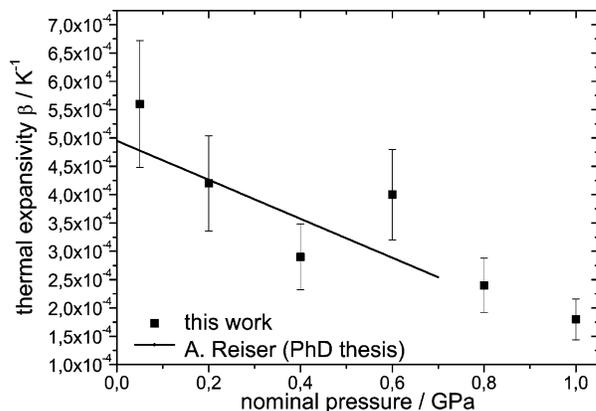


Figure 6. Summary of isobaric expansivities of liquid glycerol at $T > T_g$ in comparison with literature data from ref 65. Data are corrected for apparatus function.

reduced glass transition width is systematically lower for these cases (by about 0.01–0.02). A summary of the thermal expansivity of liquid glycerol at $T > T_g$, which is approximately equal to $\Delta\beta$, as a function of the pressure is given in Figure 6. These data are obtained after correcting data such as in Figure 2e and Figure 3c for the apparatus expansivity. The data shown in Figure 2e is calculated as the first derivative of the data in Figure 2b divided by the sample volume at 200 K and 0.050 GPa, which is 378.0 mg divided the density of 1.333 mg/mm³. The volume change of about 6 mm³ seen in Figure 2c is neglected for the purpose of calculating β since the error caused is insignificant in comparison to the reproducibility of the method (about $\pm 1 \times 10^{-4}$ K⁻¹). The increase in expansivity at the glass \rightarrow liquid transition at ~ 188 K is calculated as $\Delta\beta \approx 5 \pm 1 \times 10^{-4}$ K⁻¹ at 0.050 GPa. A similar increase of $\Delta\beta \approx 3 \times 10^{-4}$ K⁻¹ was measured on the example of a styrene-acrylonitrile copolymer at 0.050 GPa (cf. Figure 9 in ref 66). The change in expansivity $\Delta\beta$ incurred as a result of the glass \rightarrow liquid transition in the narrow temperature interval around T_g is approximately equal to β (liquid glycerol). Apparently, $\Delta\beta$ decreases with increasing pressure. Since glass-formers showing a large $\Delta\beta$ (such as *o*-terphenyl) are classified as fragile liquids, and glass-formers showing only a small $\Delta\beta$ (such as SiO₂) are classified as strong liquids,²⁷ it is tempting to associate decreasing $\Delta\beta$ with decreasing fragility. However, we note that a comparison of $\Delta\beta$ is only valid between different substances kept at the same pressure (typically 1 bar). $\Delta\beta$ typically decreases with increasing pressures for both fragile and strong substances simply since the increasing external compaction force works against the thermal expansion. The decrease in $\Delta\beta$, therefore, does not contradict the increasing fragility inferred from Figure 5.

4. Conclusions

We report a novel isobaric method of measuring the glass → liquid transition at elevated pressures up to the GPa range. As an example to show the potential of the method we study glycerol's glass liquid transition in the pressure range 0.05–1.00 GPa. The glass liquid transition at $T_g \approx 188$ K (0.050 GPa) is reversible and can be observed reproducibly in multiple heating cycles. The sharp increase of thermal expansivity amounts to $\Delta\beta \approx 5 \pm 1 \times 10^{-4} \text{ K}^{-1}$ (0.050 GPa). Varying overshoot effects observed in the thermal expansivities as well as a slight shift observed for T_g on varying cooling rate and/or pressure agree with the expectations from the theory of glasses. The pressure dependence of glycerol's glass → liquid transition is in good qualitative agreement with literature studies. We, therefore, regard this technique of observing the glass → liquid transition upon heating the glass into the liquid state at elevated pressures as a reliable tool in determining T_g and in estimating the liquid's fragility. We estimate the accuracy of our T_g to be at least ± 2 K even at high pressures. Such a technique of monitoring glass → liquid transitions not only at 1 bar but also at higher pressures needs to be employed for any substance that is not stable up to its T_g upon heating at 1 bar, e.g., HDA. With our current setup it is possible to work in the range 4 MPa–2 GPa. This covers the whole range important for the study of a possible glass → liquid transition in high pressure amorphous ices.

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