

Aging and Solidification of Supercooled Glycerol

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We experimentally investigate the solidification of supercooled glycerol during aging that has recently been observed by Zondervan et al. We find that a slow cooling at 5 K/h prior to the aging is required for solidification to take place. Furthermore, we show that the time of onset depends strongly on the aging temperature which we varied between 220 and 240 K. The nature of the solid phase remains unclear. The experiments show that upon heating the solid glycerol melts at the crystal melting point. However, rheology experiments in the plate–plate geometry revealed the growth of a soft, slushlike phase that is distinct from a crystal grown by seeding at the same aging temperature. The slushlike glycerol grows from a nucleation point at almost the same speed as a seeded crystal quenched to the same temperature, but its shear modulus is almost 2 orders of magnitude lower than the crystal phase, which we measure independently. While solidification was reproducible in the Couette geometry, it was not in the plate–plate geometry.

Introduction

Recent single-molecule optical experiments on supercooled glycerol near the glass transition have shown evidence for dynamical heterogeneities on the molecular level.¹ Most strikingly, the observed lifetime of the spatial heterogeneity is on the order of hours, about 6 orders of magnitude longer than the typical time for a glycerol molecule to reorient. Moreover, a recent experiment by Zondervan et al.² has shown that the rheology of supercooled glycerol near the glass transition exhibits a novel viscoelastic behavior after sufficient aging of the sample. This was a surprising finding, given that supercooled liquids are thought to be pure Newtonian liquids whose viscosity diverges at the glass transition temperature T_g . This non-Newtonian behavior has been conjectured to be a consequence of these microscopic heterogeneities.²

In this paper we expand on the work by Zondervan et al.,² who were restricted by their experimental setup to steady shear measurements which can cause “breaking events” that rejuvenate the sample. Moreover, they did not have optical access to the sample as it aged. In this work we address these shortcomings by performing the experiments in a rheometer.

We employ an Anton Paar MCR 501 rheometer with an environmental chamber that enables us to probe the supercooled glycerol with small strain amplitude oscillatory measurements to avoid the previously observed “breaking events” of the fragile network while measuring its response. We perform experiments first in a Couette geometry with similar dimensions as in Zondervan et al.’s study.² We monitor the linear response of supercooled glycerol as a function of aging time at different aging temperatures above the glass transition. We find that an initial slow cooling period is crucial for the formation of the solid-like state. However, the deformation of the measurement tools (apparatus compliance) may limit the maximum measurable rigidity of the sample.³ We could not ascertain whether the solid-like structure we measure in the Couette geometry is

a crystal growing in a liquid or a solid-like phase distinct from the normal crystal.

We therefore repeated the experiment in a plate–plate geometry, where gap and plate size were chosen such that the tool compliance is negligible. In addition, the sample can be optically accessed in this geometry. Surprisingly, we could not reliably reproduce the solid-like state in the plate–plate geometry, although we applied the same temperature history as in the Couette geometry. Nevertheless, we found evidence of a slushlike phase that grows from a nucleation point at the speed of the crystal phase but has a soft slushy consistency with a shear modulus about 2 orders of magnitude lower than the crystal phase. The storage modulus of the slushy phase is within an order of magnitude of the modulus found by Zondervan et al., although the aging temperatures were different (240 K vs 205 K).² When slowly heated, the slushlike phase eventually melts at the crystal melting point of glycerol which indicates that the slush either contains crystallites or turns into a crystal at higher temperatures.

Experimental Setup

In order to probe the solidification of glycerol during aging, we employed a Anton Paar MCR 501 rheometer with two measurement geometries. The first is a Couette geometry (Anton Paar CC 20) similar in dimensions to that used in Zondervan’s study:² The gap size between inner and outer cylinder is 1 mm. The inner cylinder has a radius of 10 mm and is 30.1 mm long, with a conical bottom. The compliance of the tool and the cup as stated by the manufacturer is 1.65 and 4.5 mrad/(N m), respectively. The total sample volume is about 7 mL.

Our customized plate–plate geometry consists of two parallel disks with an upper disk radius of 1.5 mm and gap sizes between 2.0 and 2.3 mm. The small radius and large gap size ensure that compliance effects are negligible, which we checked explicitly (Figure 5). Another advantage of this geometry is the optical access through the observation window of the chamber. We mounted a camera with a microscope lens outside the chamber which was focused on the sample. The sample was

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backlit with a LED behind a diffusing plate inside the chamber; the LED was turned on all the time and had no heating effect on the sample. The disadvantage of the geometry is the lower accuracy because of increased edge effects—the sample between the plates is not cylindrical but has a meniscus—and the lower sensitivity. It can only be used for samples with high moduli. Also, the sample volume, about 0.014 mL, is much smaller than in the Couette cell.

Both geometries are placed in a low-temperature environmental chamber (Anton Paar CTD 450), which allows cooling down to 173 K. The cooling is provided by a liquid nitrogen evaporation unit (Anton Paar EVU), which, coupled with the heating elements in the chamber, ensures constant temperature environment with fluctuations of around 0.1 K. The flooding of the chamber with nitrogen vapor also prevents water uptake of the glycerol sample. Because of the high consumption of liquid nitrogen (about 6 L/h), we had to change dewars every 15–20 h. Furthermore, we restricted our measurements to aging temperatures of 220 K and above, which is in contrast to the previous study in which the aging temperature was 205 K and the waiting time extended to weeks.²

A temperature probe (Anton Paar Pt 100) is located at the bottom of both the Couette and plate–plate geometry and allows the rheometer to control the temperature in the chamber (the temperature difference from the center of chamber to the wall can be up to 4 K). A more accurate, better calibrated silicon diode (Lakeshore, DT-670-CU-1.4 L) is attached directly to the cup of the Couette cell and the bottom plate of the plate–plate geometry and was used to measure the absolute temperature.

During the course of the experiment we used two ultrapure samples (99.5% purity) of glycerol from two different suppliers, Invitrogen and Fluka, and no significant differences were found between these two samples. The bottle of glycerol was sealed with Parafilm and kept in a desiccator. Both samples could be solidified in the Couette geometry.

Results

Viscosity Measurements. First we measured the viscosity of glycerol as a function of temperature in a Couette cell and a plate–plate geometry to test the accuracy of these two different geometries. In both geometries we did strain rate-controlled measurements. It is important to be cautious: when the elastic constant of the sample becomes comparable to that of the measurement cell, the compliance of the measurement device may overwhelm the deformations in the sample.³ As is shown in Figure 1, the measured storage modulus of frozen water with the Couette cell plateaus around 10⁷ Pa, which is 2 orders of magnitude below the actual shear modulus of ice (3.9 GPa).⁴ Although this compliance effect is expected in the Couette geometry, it does not affect the viscosity measurements at steady shear.³ At each data point we waited 10 min before the measurement was taken to allow thermal equilibration of the sample. As can be seen in Figure 2, the measured values of the viscosity vs temperature are in good agreement with previous measurements by Schröter et al.⁵ In case of the plate–plate geometry the viscosity values are slightly lower, which can be attributed to lower accuracy due to edge effects (see the Experimental Setup section).

Solidification and Importance of Cooling Rate. An initial slow cooling is important for glycerol to develop a solid-like structure. In order to create the solid-like state observed by Zondervan et al., we first performed the aging experiments in the Couette Cell. We found that rapidly cooling down the sample to $T = 192$ K, which is close to the glass transition temperature

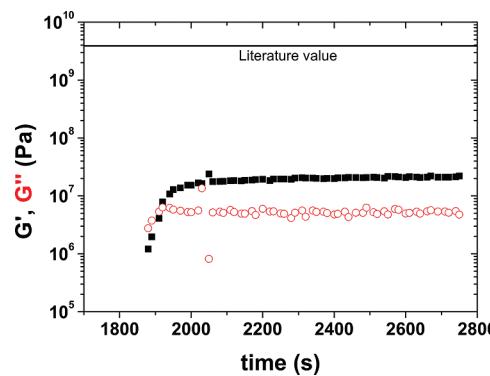


Figure 1. Measurement artifact in the Couette cell. Oscillation measurement (G' (■), G'' (○)) of ice in the Couette cell at $T = 268$ K. The oscillation test yields a storage modulus (G') that is 2 orders of magnitude lower than the actual shear modulus of ice due to tool compliance, indicating that the upper limit of the measurable shear modulus with the Couette cell is on the order of 10⁷ Pa.

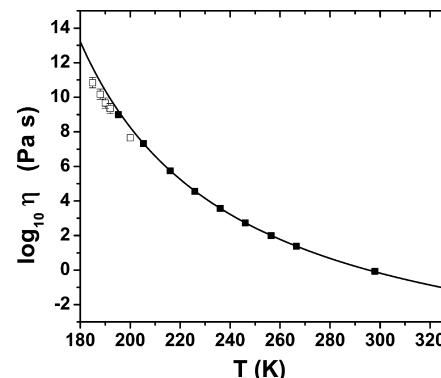


Figure 2. Dynamic viscosity measurements of glycerol. All the measurements are obtained at steady shear (strain rate controlled) on the quickly cooled liquid state of glycerol. The shear rates we used varied from 10⁻² s⁻¹ at room temperature down to 10⁻⁶ s⁻¹ at 185 K. The solid symbols (■) are taken in the Couette cell; empty symbols (□) are measurements from the plate–plate geometry. The solid line is the VFT (Vogel–Fulcher–Tammann–Hesse) fit from Schröter et al.:⁶ $\log(\eta/\text{Pa}\cdot\text{s}) = -7.1 + 1260/(T - 118)$.

$T_g = 190$ K, followed by an aging at a higher temperature, irrespective of the aging temperature, did not lead to solidification reliably. The aging has to be preceded by a slow cooling period at a rate of 5 K/h. This is also what Zondervan et al. did for technical reasons, although it was not known to them at the time that this is crucial for creating the solid-like state.

The temperature protocol that leads to reproducible solidification is as follows (see Figure 3a): First, the sample is cooled down to 260 K from room temperature within about 20 min, during which the temperature inside the environmental chamber is equilibrated. Then the sample is slowly cooled down further at a rate of 5 K/h to 192 K, which is just above T_g . After 2–3 h at 192 K, the sample is warmed up to the desired aging temperature T_a at a rate of 1 K/min. When the T_a is reached, the linear response is probed by oscillation measurements at $f = 0.1$ Hz and a low strain amplitude $\gamma = 5.3 \times 10^{-4}$. The low strain amplitude was chosen to disturb the sample as little as possible.

In Figure 3b–d we show the storage and loss modulus as a function of time for the glycerol in the Couette geometry at three different aging temperatures. In all cases, the development of a solid-like structure is evidenced by a steep increase of G' (and G'') at time t_s . This increase is only observable several hours after the final aging temperature T_a has been reached. The

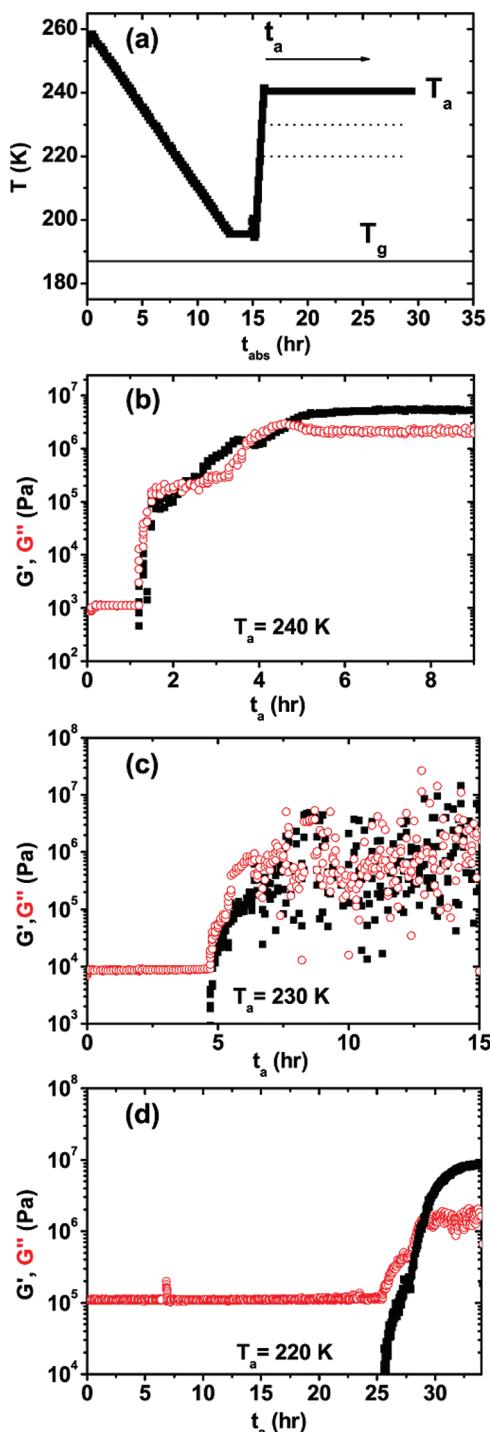


Figure 3. Aging and solidification of supercooled glycerol. (a) This is the temperature protocol used to create the solid-like state shown in (b)–(d). The sample is slowly cooled at 5 K/h from 260 K down to 192 K where it remains for 2–3 h. It is then warmed up at 1 K/min to the desired aging temperature T_a . The dotted lines indicate the different aging temperatures T_a that have been probed. Panels b–d show the linear response, G' (■) and G'' (○), of the oscillatory measurements during aging at $f = 0.1$ Hz and a low strain amplitude $\gamma = 5.3 \times 10^{-4}$ at different aging temperatures T_a : (b) $T_a = 220$ K, (c) $T_a = 230$ K (scatter of points for $t > 7$ h is not well understood and may be due to internal stresses building up upon solidification), and (d) $T_a = 240$ K. The aging time $t_a = 0$ when T_a has been reached. Note: the bump in G'' at $t_a = 7$ h is due to the changing of the dewar.

solidification time t_s increases with decreasing T_a . The curves of the moduli as functions of time are not smooth and frequently exhibit kinks, i.e., sudden increases of the time derivatives of

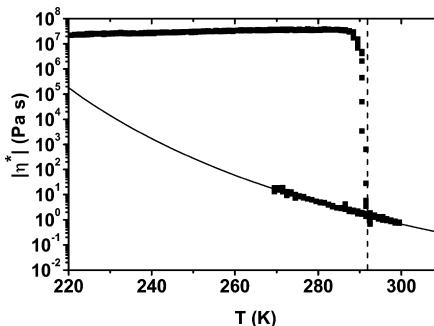


Figure 4. Modulus of complex viscosity monitored during melting and subsequent cooling. This is the same experimental run as shown in Figure 2d. After aging at 220 K, during which the glycerol has solidified, we slowly heated the sample at 15 K/h while monitoring the linear response. At the melting point of the crystal phase of glycerol $T_m = 291.75$ K,⁶ the modulus of the complex viscosity drops down to the values for the dynamic viscosity expected for liquid glycerol. Subsequent cooling from 300 K shows that the Newtonian liquid behavior is restored. The solid line is the same VFHT fit as in Figure 2.

the storage and/or loss moduli. These kinks might indicate meeting or merging events of some macroscopic solid-like clusters as they grow. Since the Couette cell is not transparent, we cannot test this.

Once the solid-like state is formed, it can be molten by heating the sample considerably. Figure 4 shows the magnitude of the complex viscosity of solidified glycerol obtained from the aforementioned procedure as a function of temperature. By warming up the sample at a rate of 0.2 K/min, we first observed a slight increase in the complex viscosity between 220 and 288 K and then a drastic drop when the temperature crossed 291.75 K, the melting temperature of the crystalline glycerol.⁶ After that, the values of viscosity followed the literature values of supercooled glycerol. When the solid-like structure has completely molten, the sample was cooled down again from 300 K at a rate of 0.2 K/min, and it behaved like a normal supercooled liquid.

The apparent shear modulus of the solid-like state, as shown in Figure 3, is 2 orders of magnitude lower than the modulus of crystalline glycerol, which is about 3.4 GPa, as derived from the transverse sound velocity in the crystal.⁷ Since the control measurements on frozen water have pointed out the compliance issue, the plateau values of the moduli of the aged glycerol we measured in the Couette geometry cannot be trusted.

Measurements in the Plate–Plate Geometry. In order to avoid complications due to the compliance of the tool, we turned our attention to the plate–plate geometry with a relative wide gap and a small radius.³ To ensure that the geometry is free of compliance artifacts, we measured the α -relaxation peak of the loss modulus in supercooled glycerol at different temperatures. After a sufficient equilibration period of the sample at each temperature, we performed an isothermal frequency scan of the complex moduli. As can be seen in Figure 5a, there is a well-defined, asymmetric peak in G'' at a frequency corresponding to the α -relaxation time similar to measurements by Jeong⁸ and Schröter et al.⁵ Moreover, the storage modulus G' at high frequencies plateaus around 3.7 ± 0.1 GPa, which agrees well with previous results.^{3,5} Furthermore, we probed the temperature dependence of the relaxation peak in G'' . As shown by earlier experiments,⁸ the complex moduli can be rescaled on a master curve (see Figure 5b), where the peak frequencies are well fit by a VFTH equation.

Surprisingly, the same temperature protocol, which worked reliably in the Couette geometry to create the solid-like state,

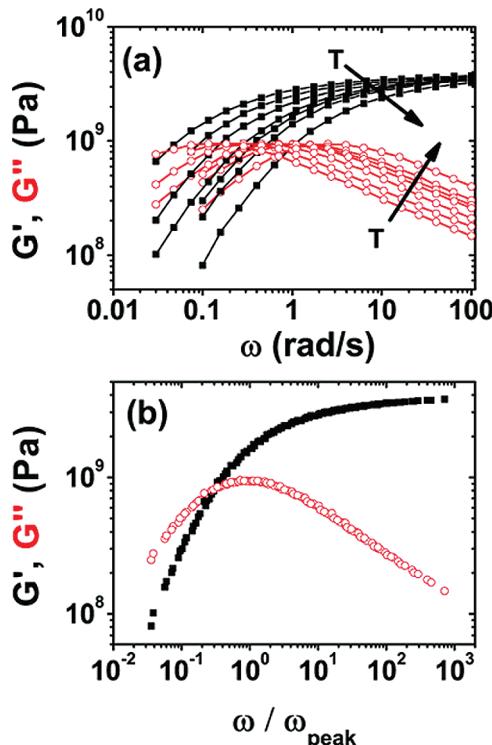


Figure 5. Relaxation peak of liquid supercooled glycerol near the glass transition (G' (■), G'' (○)). (a) Oscillation measurements in plate–plate geometry at strain amplitude $\gamma = 1.3 \times 10^{-4}$ were performed at temperatures $T = 186, 187, 188, 189, 189.5, 190$, and 191.5 K. The two arrows indicate the shift of the curves with increasing temperature. (b) Collapse of the data of (a) with the temperature-dependent rescaling of the frequency axis according to the VFT fit: $\omega_{\text{peak}} = 5.7 \times 10^{16} e^{-2856/(T-117)}$ rad/s.

could not reproduce the solid-like state of glycerol very well in the plate–plate geometry. Out of six trials only one run yielded a solid-like state. Roughening the plates with sandpaper did not help to induce slush formation. In addition, a number of cuvette cells (dimensions $1 \times 9.5 \times 45$ mm 3 , $2 \times 9.5 \times 45$ mm 3 , $5 \times 9.5 \times 45$ mm 3 , and $10 \times 9.5 \times 45$ mm 3) filled with glycerol were subjected to the same temperature protocol, and none of them showed a cloudy appearance.

As mentioned above, we did observe once the spontaneous solidification of the sample in the plate–plate geometry with our temperature protocol. During that run, a slushy phase formed at $T_a = 240$ K, as shown in Figure 6. G' and G'' showed a sudden increase once the solidification front spanned the whole gap after about 4 h aging at 240 K. However, both moduli leveled off around $\approx 3 \times 10^7$ Pa—2 orders of magnitude below the shear modulus of crystalline glycerol, which is 2×10^9 Pa (see Figure 7).

The measured speed of the solidification ($v = (1.1 \pm 0.2) \times 10^{-7}$ m/s) front is very close to the growth of the glycerol crystal at the same temperature (see Figure 7), in agreement with literature values.⁹ In addition, a frequency sweep of G' and G'' of the solidified sample shows an essentially flat frequency response over 3 decades in ω . The reason for the similar magnitude and fluctuations of G' and G'' might be slippage at the upper plate. However, when we applied a moderate normal force of 10 N to the sample in order to reduce slip, it immediately deformed and was crushed by the upper plate as shown in Figure 6. This is in stark contrast to the crystalline glycerol sample (Figure 7) that withstood up to 50 N normal force (the maximum applicable force with our rheometer)

without any plastic deformation. This clearly indicates that the slushy phase created through aging has a much lower rigidity than the ordinary crystal.

For comparison, we created an ordinary glycerol crystal and measured its rheological properties: From the previous Couette runs we could harvest crystal seeds that were scratched from the sample before it reached the melting point. These seeds were used to grow large crystals in the freezer at $T = 253$ K. To compare with the slushy phase, we seeded the glycerol sample in the plate–plate geometry that was quenched to $T = 240$ K with a few micrograms of the crystal.

By direct imaging, we measured the crystallization front that slowly spreads from the upper plate through the sample (Figure 7) at a speed of $(9.8 \pm 0.2) \times 10^{-8}$ m/s at 240 K. After 2 h, the whole sample has crystallized and the elastic moduli have jumped up. The storage moduli obtained from oscillatory measurements are centered around 2.2 ± 0.5 GPa, which is consistent with previous measurements.⁷ A subsequent strain sweep at $f = 0.1$ Hz at a normal force $F_N = 20$ N shows that the storage modulus is constant over a range of strain amplitudes, although for larger strain the elastic modulus decreases while the loss modulus increases. This is either due to slip or shear-induced rejuvenation of the solid. The measurements presented in Figure 7 show that we can reliably determine moduli of the solidified glycerol in the relevant GPa range.

Discussion

We have reproduced the solid-like state of glycerol in the Couette geometry at temperatures well above the glass transition as was reported by Zondervan et al.² We have established that an initial slow cooling period is crucial to create the solid-like state reliably. Perhaps, upon slow cooling, the molecules have enough time to locally rearrange themselves into a configuration that is more favorable for the nucleation of a solid-like structure. This would be more difficult in case of a fast cooling where the molecules are quickly arrested at temperatures close to the glass transition. Once the solid-like structures are formed in the glycerol, the rigidity of the sample increases with time. Both the waiting and the hardening times decrease with increasing aging temperature. However, the maximum moduli we could probe in the Couette geometry are of the order of 10^7 Pa due to the compliance of the measuring tool. The measurements on frozen water indeed confirmed this compliance issue, which also leaves the possibility open that the moduli of solidified glycerol may reach the GPa range.

In order to avoid the compliance issue, we switched to the plate–plate geometry, which allows us to access the sample optically and avoid the compliance artifact. Surprisingly, the same temperature protocol, which led to a solid-like state in the Couette cell in every run, did not work reliably in the plate–plate geometry. This is not understood yet. However, it should be pointed out that the Couette cell holds about 7 mL of glycerol and has an effective contact area about 2000 mm 2 , whereas the plate–plate geometry holds about 0.014 mL of glycerol and the contact surface is about 9.42 mm 2 . If the formation of the solid-like structure is nucleated from clusters whose probability depends on the volume or/and surface, this nucleation may be prohibitively unlikely in the plate–plate geometry.

The nature of the solid-like state remains unclear. It is tempting to conclude that the solid-like behavior is due to a crystal structure growing in a liquid and giving rise to a viscoelastic linear response in the temperature range of our measurements. This scenario is supported by the observations

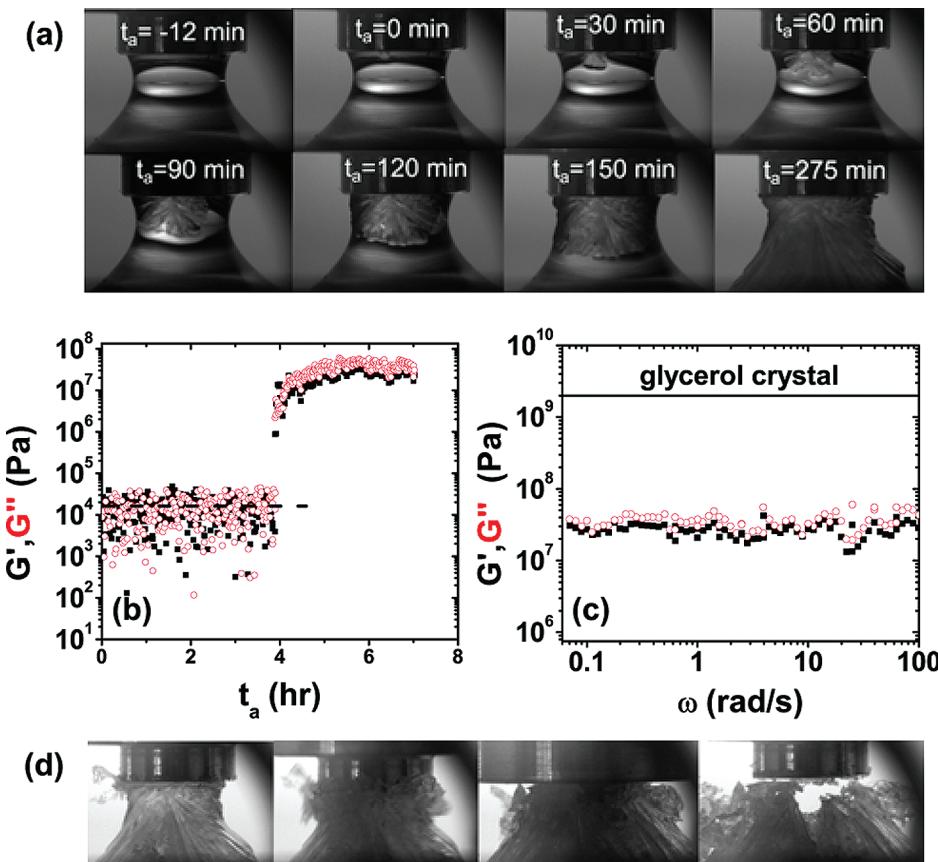


Figure 6. Emergence of the slushy phase after aging at $T_a = 240$ K. The same temperature protocol as in Figure 2a was followed. (a) Snapshots of the slushy phase at different times, showing a crystallization-like front moving at $v = (1.1 \pm 0.2) \times 10^{-7}$ m/s. (b) G' (■) and G'' (○) as a function of time (frequency $f = 0.1$ Hz, strain amplitude $\gamma = 7 \times 10^{-4}$). The noise floor is denoted by the dotted line. (c) Frequency sweep of G' (■) and G'' (○) at $t_a = 7$ h, showing a flat frequency response over 3 decades. The line indicates the storage modulus of crystalline glycerol. (d) After the oscillation measurement, a normal force of 10 N is applied, and the slushy phase immediately deforms plastically indicating a low rigidity. The first picture on the left shows the sample just before the crushing, the next two pictures are during the crushing event, while in the last picture the upper plate has been retracted. Note that the sample could withstand a normal force of 2 N without plastic deformation.

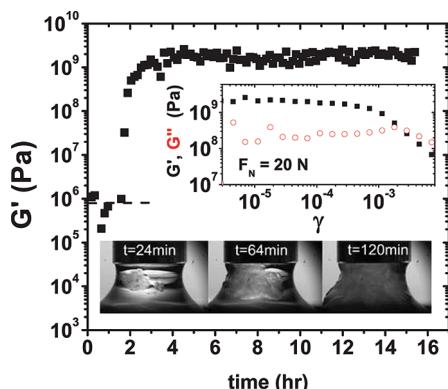


Figure 7. (a) Measurement of G' of supercooled glycerol at 240 K in plate–plate geometry seeded with a crystal, $f = 0.1$ Hz, $\gamma = 3.5 \times 10^{-6}$, and gap is 2.0 mm. The noise floor is denoted by the dotted line. The inset shows strain sweep (G' (■), G'' (○)) at 0.1 Hz with applied normal force $F_N = 20$ N measured 15.4 h after seeding the crystal. Also shown are snapshots of the growing crystal at different times as indicated. The crystal front grows with speed $v_c = (9.8 \pm 0.2) \times 10^{-8}$ m/s. Once the crystal spans the two plates, G' rapidly increases.

that the growth rate from a nucleation point and the melting temperature of the solid-like structures are similar to those of the crystal. However, the shear modulus of the slushy phase is 2 orders of magnitude lower than that of the crystal. Moreover, this slushy material can be easily deformed plastically. If the solid-like parts of the slushy phase are small crystallites, their

growth appears to be inhibited. This could be because the crystallites are smaller than the nucleation radius or because of frustration. These crystallites are loosely organized and coexist with a liquidlike fraction, leading to an overall smaller rigidity than the polycrystals (see Figure 7). The images of the crushed sample (Figure 6d) also suggest the existence of such crystallites on a larger scale. However, the crystalline structure of this slushy phase is still speculative at this point and would have to be proved by a structural analysis, e.g., X-ray or neutron scattering. It is reasonable to assume that the solid-like states formed in the Couette cell upon aging at 220, 230, and 240 K, after undergoing the same temperature protocol, are also slushlike and will turn into a crystal state upon heating, which is evidenced by the observed melting behavior at the crystal melting point. We believe that the solid-like structure formed by seeding a quenched glycerol sample is a crystal since its shear modulus is of the order of GPa, close to that of crystalline glycerol deduced from sound velocity measurements.⁷ Moreover, it can be deformed elastically. To our knowledge, this is the first time the shear modulus of polycrystalline glycerol has been directly measured.

A similar solid-like behavior was found earlier in triphenyl phosphite (TPP), another molecular liquid, well-known to exhibit an intriguing glacial state, an apparently amorphous state different from the glass and the ordinary liquid.^{10–13} There are some striking similarities between the slushy state of supercooled glycerol and the glacial state of TPP. For example, the

rheological experiments on the glacial state of TPP shows that the maximum G' is order of 10^6 Pa,¹² close to 10^7 Pa of the slushy phase of glycerol. Both moduli are far below their respective crystalline moduli. Upon heating, the glacial state of TPP turns into a crystal,^{11,12} which also happens to the solidified glycerol since it melts at the melting point of crystalline glycerol. The structural description of the glacial state of TPP is still under debate. The evidence that the glacial phase is a mixture of microcrystallites and nontransformed supercooled liquid came from the measurements performed at higher temperatures (216–235 K),¹⁴ whereas the experiments at a lower temperature (213 K) suggest that the glacial state is a homogeneous glassy state of a denser liquid free from microcrystallites.^{12,15} It would be interesting to do the aging measurements on glycerol at lower temperatures. However, the kinetics associated with this aging process for glycerol appears to be much slower than that of TPP, which makes the experiments e.g. at $T = 205$ K impractical.² It still remains an open question if the scenario of the glacial phase in TPP carries over to supercooled glycerol. If so, the time scales of forming the glacial state are vastly different.

Conclusion

We can reproduce the solid-like state of glycerol in the Couette geometry reliably with our temperature protocol which involves an initial slow cooling period prior to the aging, but not in the plate–plate geometry (except for one run out of six). The observed viscoelastic behavior seems to be related to a crystal-like structure growing in a liquid in the probed temperature range, 220–240 K. However, this crystal-like structure can vary considerably in its rheology. The slushy phase, which grew from a nucleation point after slow cooling and subsequent aging at 240 K, behaved quite differently from the crystal that was created by seeding a glycerol sample quenched to the same aging temperature. The slushy phase is 2 orders of magnitude softer and can easily be deformed plastically, whereas the seeded sample has a shear modulus of ≈ 2 GPa and can only be elastically deformed. Whether the slushy state of glycerol shares the same structural origin as the glacial state of TPP remains an open question. Nevertheless, the cooling rate emerges as a crucial parameter in studies of glycerol at temperatures near

the glass transition and appears to affect the structure and dynamics on the molecular level.

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Supporting Information Available: Movies for the solidification (movie1.avi) and subsequent “crushing” (movie2.avi) at $T = 240$ K after slow cooling as shown in Figure 6 as well as the crystallization through seeding at the same temperature after fast cooling (movie3.avi) as shown in Figure 7; an example of a constant stress measurement that shows the nonlinear behavior of strain vs time similar to what Zondervan et al. observed. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- (1) Zondervan, R.; Kulzer, F.; Berkhouit, G. C. G.; Orrit, M. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 12628–12633.
- (2) Zondervan, R.; Xia, T.; van der Meer, H.; Storm, C.; Kulzer, F.; van Saarloos, W.; Orrit, M. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 4993–4998.
- (3) Schröter, K.; Hutcheson, S. A.; Shi, X.; Mandanici, A.; McKenna, G. B. *J. Chem. Phys.* **2006**, *125*, 214507.
- (4) Cox, J. L., Ed.; *Natural Gas Hydrates: Properties, Occurrence, and Recovery*; Butterworth: London, 1983.
- (5) Schröter, K.; Donth, E. *J. Chem. Phys.* **2000**, *113*, 9101–9108.
- (6) Weast, R. C., Ed.; *Handbook of Chemistry and Physics*; The Chemical Rubber Co.: Boca Raton, FL, 1968.
- (7) Bermejo, F. J.; Criado, A.; de Andres, A.; Enciso, E.; Schober, H. *Phys. Rev. B* **1996**, *53*, 5259–5267.
- (8) Jeong, Y. H. *Phys. Rev. A* **1987**, *36*, 766–773.
- (9) Tammann, G.; Jenckel, E. Z. *Anorg. Allg. Chem.* **1930**, *193*, 76–80.
- (10) Ha, A.; Cohen, I.; Zhao, X. L.; Lee, M.; Kivelson, D. *J. Phys. Chem.* **1996**, *100*, 1–4.
- (11) Cohen, I.; Ha, A.; Zhao, X. L.; Lee, M.; Fischer, T.; Strouse, M. J.; Kivelson, D. *J. Phys. Chem.* **1996**, *100*, 8518–8526.
- (12) Tanaka, H.; Kurita, R.; Mataki, H. *Phys. Rev. Lett.* **2004**, *92*, 025701–025704.
- (13) Kurita, R.; Tanaka, H. *Science* **2004**, *306*, 845–848.
- (14) Hédoux, A.; Guinet, Y.; Derollez, P.; Hernandez, O.; Lefort, R.; Descamps, M. *Phys. Chem. Chem. Phys.* **2004**, *6*, 3192–3199.
- (15) Kurita, R.; Shinohara, Y.; Amemiya, Y.; Tanaka, H. *J. Phys.: Condens. Matter* **2007**, *19*, 152101.

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