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Glass in a stretched state formed by negative-pressure vitrification: Trapping in and relaxing out

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To explore the influence of the attractive side of the intermolecular potential on liquid structure and dynamics, we are studying liquids under negative pressure. To preserve and characterize the interesting stretched configurational states, we have vitrified the glass-forming liquid *o*-terphenyl under ~80-bars negative pressure. The *ambient* pressure relaxation to normal volume at T_g of the stretched glass shows pronounced differences from the relaxation of the corresponding compressed state, suggestive of an increased "fragility" of liquids under tension.

One of the interesting but less exploited aspects of the vitreous state is its capacity to preserve information on the structure and thermodynamics of liquids in exotic states so that these states can later be studied at leisure under ambient pressure and/or temperature conditions. Examples are (i) the determination of the *liquid* state compressibility of liquid SiO_2 at 1600 °C via *ambient temperature* study of the nonpropagating density fluctuations which are frozen in at the glass transition[1,2] and (ii) the recent first observation of 6-coordinated Al^{3+} in an aluminosilicate glass by *ambient pressure* NMR study of the structure formed and frozen in by vitrification at 80-kbar pressure and ~1000 K.[3,4]

In the present Rapid Communication we report the use of the same principle to preserve, for ambient pressure study, the *stretched* state of a liquid held under negative pressure prior to vitrification.

Negative pressure states of liquid systems have been given very little systematic study despite the predicted existence at negative pressure of an interesting mechanical instability[5,6] which must have, associated with it as precursor to the phase transition, unusual and interesting liquid-state properties. For instance, simple equations of state such as the van der Waals equation and the Berthollet equation, predict infinite ambient temperature compressibilities for toluene at the moderate negative pressures of -155 and -750 bars, respectively. Indeed diverging compressibilities have been observed in computer simulation studies of stretched liquids.[7]

We believe this is an interesting and important region of metastable liquid-state behavior and one which deserves systematic exploration. It is in this region that the attractive side of the minimum in the intermolecular potential begins to dominate the liquid behavior. Likewise, this is where anharmonic effects should become rather important and where the breakdown of some approximations of liquid behavior based on repulsive potential dominance should fail in a diagnostically useful manner. While there have been many studies aimed at determining the tensile limit for liquids,[8-10] there has been little effort devoted to the question of physical properties of a liquid under negative pressure, the only recent effort having been the clever *PVT* measurements of Henderson and Speedy[10,11] on water to -220 bars.

Since the concept of negative pressures is frequently greeted with some skepticism we judged that such studies would gain in credibility if we could first produce a vitreous phase under negative pressure, so that its expanded state could subsequently be examined at *normal* pressure. In this way its unusual features could be identified and the conditions of its formation (i.e., the negative pressure, i.e., tension, acting on it at the time of formulation) deduced in a fairly unambiguous manner. We have chosen *o*-terphenyl as test substance because of its convenient glass transition temperature, -33 °C and the extent of its prior characterization.[12-15]

The experiment we have performed to vitrify *o*-terphenyl under tension is simple in conception and, except for degassing problems, not difficult in execution. It is an adaptation of the idea of Berthollet[16] for creating static negative pressures in liquids.

The liquid *o*-terphenyl to be vitrified is contained in the lower section of the pyrex glass tube illustrated in Fig. 1(a), which had previously been baked under vacuum to degas the tube walls. The upper section was then filled with an immiscible noncrystallizing liquid of lower glass

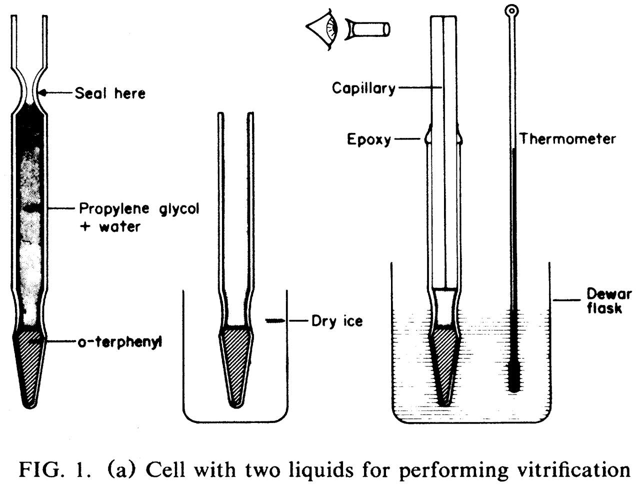

FIG. 1. (a) Cell with two liquids for performing vitrification under tension; (b) preservation of stretched glass at ambient pressure; and (c) conversion to dilatometer for study of warm-up behavior of stretched configuration.

transition temperature. In the present case a mixture of water and propylene glycol, 1:3 by volume, was found suitable.

The tube was evacuated and subjected to ultrasonic agitation to degas each of the liquid layers as thoroughly as possible, and was then sealed off a little above the $H_2O \cdot 3PG$ meniscus. The whole tube and contents were then carefully heated until the combined expansion of the two liquids just eliminated the free space at the top of the tube.

On cooling, the tendency of the two liquids to resume their original combined volume is resisted by the free energy barrier to nucleation of a (nanoscopic) bubble,[17] since the molar free energy of molecules near a bubble surface is higher than for the bulk liquid. Since a liquid near zero pressure is as "unexpandable" as it is incompressible, the failure to resume its original volume has a large effect on the pressure inside the liquid. During cooling this latter must pass through zero, as Berthollet argued long ago,[16] and become negative in order to generate the driving force to breach the free-energy barrier to nucleation. When nucleation occurs (usually at some single point within the liquid; hence by a heterogeneous mechanism) the sudden creation of a bubble of about the size of the original vapor gap (for the same temperature) produces an audible "ping."[16] The approximate negative pressure preceding the bubble formation can be obtained from the isotropic tension needed to stretch the liquid by the volume ΔV of the bubble formed

$$\Delta V = V_0 \kappa_T (1-p) , \qquad (1)$$

where κ_T is some volume average over the compressibility of the two liquids and can be determined from a calibrating positive pressure volumetric measurement. (The same measurement on *pure* o-terphenyl samples, $\kappa_T = 6.5 \times 10^{-4}$ bars^{-1},[15] prepared in the same way, suggests that cavitation occurs at ~ −70 bars.)

With such observations as a basis for proceeding, the lower section of the tube containing the o-terphenyl was plunged into a liquid-nitrogen bath just before cavitation during cooling was to occur, so as to vitrify the o-terphenyl under maximum tension. (Crystallization of o-terphenyl never occurs under these conditions.) The cooling of the upper section was then continued until cavitation occurred. Maintaining the temperature of the lower section below the o-terphenyl T_g, the tube was then broken [Fig. 1(b)] and a capillary tube was inserted and sealed in place with epoxy resin (while taking care to avoid any air gaps). The still-liquid H_2O/PG rose in the capillary tube to create a dilatometer [Fig. 1(c)] with which the volumetric behavior in the o-terphenyl during warming above T_g could then be monitored. The dilatometer thus formed was placed in −60 °C acetone in a Dewar flask and the meniscus position level h recorded during a slow temperature rise at 0.5°/min. The observations are shown in Fig. 2(a) (solid circles).

The change of slope at ~ −33 °C in Fig. 2(a) corresponds to the return to metastable liquid equilibrium; hence, to the release of all of the state of tension frozen in during vitrification under negative pressure and preserved, when the tension was broken, by the immobility of the vitreous state. The magnitude of the excess volume frozen-in can be directly observed by requenching the now-normal pressure o-terphenyl under the same quenching conditions as before and observing the difference in h at −60 °C, and during reheating. This plot is shown as open triangles in Fig. 2(a). Note that above T_g the two plots are identical as should, of course, be the case. The change in slope corresponds to a change in expansion coefficient at T_g, $\Delta\alpha$, of 3.9×10^{-4} K^{-1}, in reasonable agreement with the

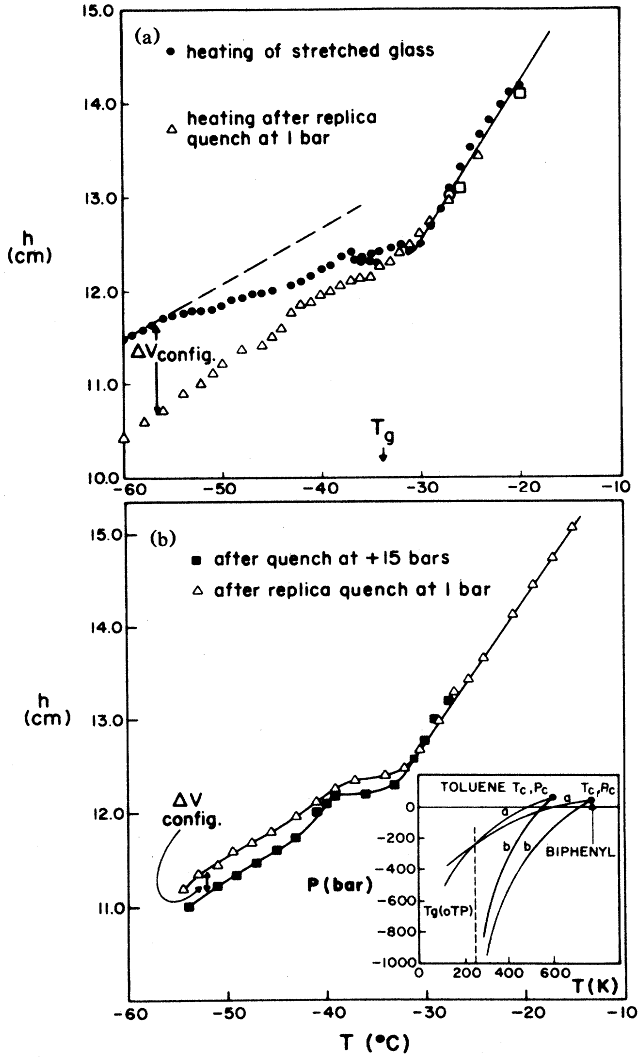

FIG. 2. (a) Dilatometer meniscus height h vs T during slow warm-up of stretched o-terphenyl glass compared with that of the same sample vitrified immediately after initial warm-up by the same quench procedure but under normal pressure. The change in slope for the normal pressure case at −30 °C corresponds to that expected from the known change in expansion coefficient at the (nonergodic ↔ ergodic) glass transition. (b) Same as for (a) except for glass vitrified under positive pressure of 15 atm. Inset: Stability limits for $T < T_c$ calculated from the van der Waals (curve a) and Berthollet (curve b) equations for two liquids related to o-terphenyl by ring number (biphenyl and toluene) for which critical constants are available (Ref. 19).

value 4.5×10^{-4} K^{-1} obtained using techniques more suited to the measurement.[13,18] The participation of some low-α PG/H_2O in our measurement will lower our value.

Knowing the capillary dimensions and the volume of *o*-terphenyl, the difference in h, marked "ΔV config." in Fig. 2, can be converted to a "stretching fraction" which is a measure of the fractional increase in volume $\Delta V/V$ at T_g maintained at the negative pressure of the original vitrification. [ΔV actually contains two components, a configurational component which has a long relaxation time and an elastic component involving bond stretching which has a very short (~ps) relaxation time. The latter would be lost at the moment when cavitation was provoked (after the vitrification step) except for the fact that the vitrified *o*-terphenyl apparently continued to adhere to the cell wall.] The stretching fraction in our experiment proves to be 0.004. Knowing the compressibility of *o*-terphenyl at T_g (Ref. 17) and assuming it to be the same on either side of the zero pressure line, we may calculate, using Eq. (1), the pressure acting on the *o*-terphenyl as it vitrified. This yields $P=-76\pm10$ bars. Since the compressibility of molecular liquids is only ~75% configurational,[15] the ΔV observed would be smaller if the *o*-terphenyl were in droplet form, or if in our experiment it cracked away from the cell walls before the dilatometry were carried out. Since partial cracking and consequent elastic relaxation cannot be excluded, there is an uncertainty in our estimated negative pressure at vitrification. -76 bars is a minimum value.

-76 bars is a substantial fraction of the theoretical tensile limit, ~-280 bars at T_g (240 K) obtained from the van der Waals equation

$$p=RT/(V-b)-a/V^2 \qquad (2)$$

[using the condition $(\partial p/\partial V)_{T=240\,\mathrm{K}}=0$] for the liquid closest in character to *o*-terphenyl for which the critical constants (hence, the constants a and b) are available, viz. biphenyl.[19] It is a smaller fraction of the limiting pressure, -1550 bars, calculated from the Berthollet equation of state

$$p=RT/(V-b)-a/V^2T \qquad (3)$$

for the same liquid [a and b the same constants as in Eq. (2)]. The locus of instability points calculated from these equations between T_c and $\sim T_g$ is shown for biphenyl and also toluene in the inset to Fig. 2(b). An analysis by Benson and Gerjuoy[20] suggests that the van der Waals and Berthollet equations, respectively, underestimate and overestimate the tensile limit, so the true limiting negative pressure at 240 K is probably of the order of -700 bars for biphenyl, perhaps less for *o*-terphenyl (see Fig. 2 inset and Ref. 19). In any event, the tensile stress at vitrification achieved in the present work is much larger than most static values reported for molecular liquids,[6] and is quite sufficient for the purpose of our study.

Figure 2 clearly establishes the existence of an ambient pressure, mechanically stable, amorphous state which could only have been produced in the presence of physically meaningful negative pressures. At the same time we must recognize that a glass in tension can also be produced by fast quenching from the liquid state—indeed, it is the tension in the interior of the soft glass "tears" produced by vitrifying the exterior skin at just the right temperature to avoid interior cavitation on final cooling, which is the secret of the centuries old "Prince Rupert's drops" (which implode on breaking off the tail of the droplet—as many visitors to Venice's island glassblowers have experienced). Even the uniform cooling of a thin section of glass through T_g at a very fast rate can produce a ΔV as great as we have produced. However, many experiments[21] have established that a glassforming liquid explores different aspects of its potential-energy surface under the influence of pressure and temperature—different degrees of freedom are involved[22]—so the glass we have produced by vitrifying under controlled negative pressure conditions will have unique features; see below.

To achieve larger negative pressures, where the expected divergence of the compressibility would be manifested and hence where more extreme and interesting expanded structural states could in principle be frozen-in, we will have to identify and eliminate the residual sources of heterogeneous nucleation which permit bubble nucleation at -75 bars, or else develop microsample techniques analogous to those which permit supercooled water studies to $-40\,^\circ$C,[23] or superheated water studies to $280\,^\circ$C,[6,9,17] at ambient pressures. For instance, there are reports of behavior of microscopic aqueous inclusions in minerals which imply that very large negative pressures may be attained.[24]

To add further credence to what is already clear from Fig. 2, a third quench has subsequently been performed, this time while the tube contents (a second tube and sample of volume comparable to the first) were under a positive pressure of ~15 bars (conveniently supplied by a commercial gas cylinder). The warmup trace for this glass, again after release of the pressure while *o*-terphenyl was below its T_g, is shown in Fig. 2(b) (filled squares). The displacement from the trace for the sample quenched at normal pressure is entirely consistent with that for the stretched liquid at the vitrification pressure estimated above. The observed displacement of the positive-pressure-quenched glass from the ambient pressure case can be used as an alternative means of estimating the vitrification pressure for the stretched sample once results have been scaled to the same sample volume (via the liquid-state expansivity). Indeed, it may be more reliable since a contribution from the elastic part of the compressibility, which caused uncertainty in the previous estimate if cracking occurred, is now already compensated by presumed equivalent behavior in the calibrating sample. This estimate yields $P=-69\pm10$ bars for the stretched glass as it vitrified, in reasonable agreement with the earlier estimate. We should make a comment here on the pressure dependence of T_g, which has been measured for *o*-terphenyl.[25] T_g increases by 20 K per kilobar. Thus the present pressures, even if applied during measurement would barely affect T_g.

The change in structure achieved by vitrification at -70 bars is far too minor to detect by scattering or spectroscopic techniques. However, the great sensitivity of transport and relaxation properties of viscous liquids to their structural states allows us to discuss some interesting aspects of the behavior of liquids which are exploring the attractive side of their interaction potentials. We compare the temperature range in Figs. 2(a) and 2(b) over which the stretched and densified glasses return to equilibrium. In so doing we are in effect comparing the spread of relaxation times (or the departure from exponentiality of the volume relaxation function) for compressed and stretched states. Figure 2(a) shows that during warming from $-60\,^{\circ}\mathrm{C}$ the "stretch fraction" is lost over a wide range of temperatures from $-55\,^{\circ}\mathrm{C}$ up to the glass transition at $\sim -33\,^{\circ}\mathrm{C}$ where, for our heating rate, the liquid should be in complete internal equilibrium. Comparing with the ambient pressure and positive pressure quenched cases which are of familiar form,[21,22] this suggests that a broader spread of relaxation times, with many fast elements compared with the average value, characterize the stretched glass. The *average* relaxation time according to light scattering measurements[25] should be $\sim 10^3$ sec at T_g ($-33\,^{\circ}\mathrm{C}$) and, by extrapolation, should rise to 10^9 sec by $-50\,^{\circ}\mathrm{C}$; yet despite this vanishingly small average time, some substantial part of the structure is relaxing on a time scale of seconds at this temperature.

Since *o*-terphenyl is already near the limit of "fragility"[26] for liquids (fragility implies high E_{act}/T_g, broad spread of relaxation times, and rapidly degrading intermediate-range order) there is a suggestion in the latter observations from Fig. 2 that fragility may be a sensitive function of pressure in the negative pressure (expanded volume) regime. Indeed, this would be consistent with the *decreases* in fragility observed for liquids at the other extreme. For instance, liquid $\mathrm{SiO_2}$ at the "strong" extreme has, as a consequence of its tetrahedral network structure, an intermediate-range order which *increases* under isotropic tension.[27] Conversely it becomes more fragile with *positive* pressure increases.[27] Increases in fragility imply increases in mobility at fixed T/T_g. This leads us to predict rapid increases of diffusivity and reorientation rates with increasing negative pressure in molecular liquids, a prediction which should be readily tested by NMR studies using established strengthened glass sample cell techniques.[28] Rapid increases in crystallization rates, reflecting increased diffusivities, have indeed been reported for samples of selenium crystallizing under conditions which the reporting authors[29] believed would throw the system into tension.

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[19] For biphenyl $T_c = 495\,^{\circ}\mathrm{C}$, $P_c = 31.8$ atm (leading to van der Waals equation constants $a = 52.79$ $\mathrm{l^2 atm/mol^2}$, $b = 0.2480$ l/mol) according to R. C. Weast [*Handbook of Chemistry and Physics*, 49th ed. (Chemical Rubber Co., Cleveland, 1969), p. F-64]. We note, however, that the value of b is larger than the volume per mole of biphenyl at ambient temperature showing that the van der Waals equation, and also the Berthollet equation, Eq. (3), are (not surprisingly) too simple to describe the whole liquid range of a complicated asymmetric molecule. D. Ben-Amotz has recently pointed out to us that a zero parameter refinement of the van der Waals equation based on the Carnahan-Starling equation for hard spheres [J. Chem. Phys. **51**, 635 (1969)] considerably improves the high-density behavior of the equation of state. Calculations by Ben-Amotz give spinodals intermediate between those of Van der Waals and Berthollet equations, viz. -475 bars for toluene and -685 bars for biphenyl at 250 K.

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