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Sub- T_g features of glasses formed by cooling glycerol under pressure - additional incompatibility of vibrational with configurational states in the depressurized, high density glass

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Abstract

The vibrational state of a glass is naturally incompatible with its configurational state, which makes the glass structurally unstable. When a glass is kept at constant temperature, both the vibrational and configurational states of a glass change with time until (equilibrium) liquid state is reached, and the two states become compatible. The process, known as structural relaxation, occurs at a progressively higher rate during heating and the properties of a glass change accordingly. We add to this incompatibility by depressurizing a glass that had been formed by cooling a liquid under a high pressure, p , and then investigate the effects of the added incompatibility by studying thermal conductivity, κ , and the heat capacity per unit volume ρC_p of the depressurized glass. We use glycerol for the purpose, and study first the changes in the features of κ , and of ρC_p during glass formation on *cooling* under a set of different p . We then partially depressurize the glass and study the effect of the p -induced instability on the features of κ and ρC_p as the glass is isobarically heated to the liquid state. At a given low p , the glass configuration that was formed by cooling at high- p had a higher κ than the glass configuration that was formed by cooling at a low p . The difference is more when the glass is formed at a higher p and/or is depressurized to a lower p . On heating at a low p , its κ decreases before its glass-liquid transition range is reached. The effect is the opposite of the increase in κ observed on heating a glass at the same p under which it was formed. It is caused by thermally-assisted loss of the added incompatibility of configurational and vibrational states of a high- p formed glass kept at low p . If a glass formed under a low- p is pressurized and then heated under high p , it would show the opposite effect, i.e., its κ would first increase to its high p value before its glass-to-liquid transition range.

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INTRODUCTION

A glass is usually formed by supercooling a liquid at ambient pressure, and it inherits the structure of its (metastable) supercooled liquid at the glass formation temperature, T_{vit} at that pressure. A glass of the same material can be formed also by pressurizing a liquid isothermally, and in this case it inherits the denser structure of its metastable liquid at glass formation pressure, p_{vit} . The structure and density fluctuations that characterize a liquid become kinetically arrested at T_{vit} , isobarically in the first case, and at p_{vit} isothermally in the second case. So, different cooling rates, $q_c (= dT/dt)_p$, produce different glasses and different pressurizing rates, $(dp/dt)_T$, would produce yet different glasses. We report a study by using a mixed temperature-pressure, $T - p$, protocol in which a liquid under different p is cooled to form glass at a rate lower than used in studies at ambient pressure; the glass at a low T is partially depressurized and heated at a slow rate at fixed low p .

The configurational state of a glass, which becomes fixed at $T < T_g$, is naturally unstable, and slowly evolves towards the equilibrium configuration of its metastable liquid. This process involves vibrational motions and their frequency also changes by the gradually changing configurational state. We regard it as a consequence of natural incompatibility of the configurational and vibrational states of a glass. (Both the vibration and configurational contribution to a property tends to zero on cooling a metastable liquid towards 0 K, but only the vibration contribution does so for a glass.) At a fixed T , the two states mutually approach a compatible state spontaneously with time and the glass ultimately becomes metastable liquid. (The stable phase is the crystal.) This is observed as spontaneous change in the properties of a glass continuously with time,^{1,2,3,4,5,6} a process known as physical aging, structural relaxation or structure stabilization,^{2,3,4,5,6} and we use these terms interchangeably. At a given T , the entropy, enthalpy and volume of a glass is higher than that of its metastable liquid at that T , and when kept at a fixed T , the glass tends to approach the low-entropy, enthalpy and volume state of its metastable

liquid,^{1,2,3,4,5} whose properties can be directly measured only when the time period for measurements is much longer than the structural relaxation time.

When a glass is heated at a fixed rate, $q_h = (dT/dt)_p$, the rate of structure stabilization increases with increase in T and its properties change more rapidly. Thus the effects of structure stabilization can be studied more conveniently by continuous heating in a shorter time than by aging at a fixed T , but it does require that changes with both time and temperature be taken into account, which introduces approximations. In calorimetric studies on continuous heating of glasses, the effects of structure stabilization appear first as a broad minimum in the heat capacity, C_p , then a sigmoid shape endothermic rise and an endothermic peak (overshoot) before the liquid state reached.^{2,3,4,5,6,7,8,9} These features contain the effect of increase in both time, t , and temperature, T , which is taken into account in analyzing the data, albeit with some approximations. The method requires less time period than obtaining data during isothermal aging.^{2,3,4,5,6} Casalini and Roland¹⁰ have shown that decrease in the dielectric strength of the β or the Johari-Goldstein relaxation measured in a relatively short time after a long-time isothermal aging may be used to follow the overall aging effects on the properties of glasses.

Tammann and Jenckel¹¹ had originally found that a glass formed at a high p has a higher density at low p than a glass formed at low p . The subject was briefly reviewed by Weitz and Wunderlich¹² by Brown *et al.*¹³ and by Johari¹⁴, the last providing extensive references to previous studies of glasses formed under high pressure and studied at 1 bar (0.1 MPa) pressure. In contrast, Bree *et al.*¹⁵ found that, in general, densification affects the thermomechanical properties only slightly. These studies led to investigation of the effects of different T , p routes on glass formation and glass local dynamics¹⁶ and on local “amorphous structure” ordering¹⁷ in polymer glasses. In addition to the normal p - T protocol, different glasses form also when a liquid kept under different high p is cooled at different rates. Here we use some of these protocols to produce glasses of *density*

higher than that of the metastable liquid and thus introduce a further incompatibility of the vibrational and configurational states in the structure of a glass. We then study loss of this incompatibility during heating at low p .

Phonon propagation in materials is usually studied by measuring their thermal conductivity, κ , a property of considerable academic interest because the phonon properties depend upon a materials structure. It is also of much practical importance in systems where heat generated by frictional, electrical, chemical or radioactive processes is to be either preserved or to be dissipated, and in cryogenic systems in which the heat transfer from the surroundings is to be minimized. Steady-state measurements have shown that when the rate of density and structure fluctuations becomes less than q_c of a liquid, the liquid become kinetically arrested on the time scale of one's measurements, and the slope of κ against T , $(d\kappa/dT)_p$, typically changes sign from negative to positive, and a glass forms. On heating a glass, when density and structure fluctuations begin to contribute on the time scale of heating, the slope of the κ against T plot changes from positive to negative. The temperature at which the sign of $(d\kappa/dT)_p$ changes depends upon q_c of the liquid and the heating rate, q_h , of the glass, and the T -range over which the sign changes is expected to show hysteresis on the cooling and heating paths. In dynamic measurements,^{18,19} the slope inversion feature is overwhelmed by a peak in κ on both the cooling of liquid and heating of glass.¹⁸

We previously reported a detailed study of glycerol by measuring its κ and heat capacity per unit volume, ρC_p , where ρ is the density, over a T range of 110 K- 300 K and p range from 0.1 MPa to 0.5 GPa.¹⁸ In that paper we provided general introduction to the subject of thermal conductivity, as well as a discussion of the auxiliary features of κ and ρC_p which extend into the liquid-glass-liquid transition range.¹⁸ In one experiment of that study, we found that glycerol glass that had been previously formed by cooling under a high p and then was measured at a low p had a

significantly higher κ than the glycerol glass formed by cooling at a low p and measured at the same low p . On heating at a fixed low p its κ decreased, instead of increasing, prior to reaching the glass to liquid transition range at that p . The effect on κ observed in that study is analogous to the effect observed in calorimetry when a glass formed at a high p showed, on heating at 0.1 MPa pressure, a sub- T_g endothermic peak in C_p before the T - range of glass-liquid transition at 0.1 MPa pressure was reached.^{12,13} On the basis of that sub- T_g endotherm, one of us concluded¹⁴ that the corresponding endotherm previously observed on heating annealed high-density solid water had been mistaken as a second T_g of water, and that this high-density solid water is an ill-defined state.²⁰ The intriguing nature of the above-mentioned sub- T_g decrease in κ made it necessary to study this feature in detail by varying the T and p protocol for glass formation as well as the protocol for studying the glass formed. It also required a corresponding study of ρC_p measured in the same experiment as κ .

The purpose of this paper is to use κ and ρC_p for investigating the nature of the sub- T_g phenomenon observed when a glass made at one pressure is studied at another pressure. We chose glycerol because we know its crystallization and other transformations from a previous study.¹⁸ There we also mentioned the technological importance of glycerol as well as its use as an environment-friendly lubricant both in the usual size mechanical and micromechanical devices in which dissipation of heat of friction by thermal conduction is important at high pressures transitorily reached during their operation.¹⁸ We focus on the changes in phonon propagation when the structure of a glass formed by cooling a liquid under a certain p stabilizes under a different p .

II. EXPERIMENTAL METHODS

Glycerol, puriss. p.a., ACS reagent, anhydrous, dist., of 99.9 % GC purity, with the main impurity being 0.07% H₂O (Karl Fischer), was purchased from Sigma-Aldrich and is the same as

used in Ref. 18. The transient hot-wire method was used to measure κ and ρC_p with estimated inaccuracies of $\pm 2\%$ in κ and $\pm 5\%$ in ρC_p .^{21,22} The hot-wire probe was a 0.1 mm in diameter Ni-wire which was inserted in a custom-made, ca. 15 mm deep and 39 mm internal diameter, Teflon[®] sample cell. The cell was filled with liquid glycerol and sealed with a tightly fitting Teflon lid. It was mounted on a bottom piston and inserted in a pressure cylinder of 45 mm internal diameter. The whole assembly was thereafter transferred to a vacuum chamber placed in a hydraulic press, which supplied the load. The vacuum chamber eliminates frost formation, which reduces the friction between the piston and pressure cylinder. Temperature was varied by heating or cooling the whole pressure cylinder by using a resistive heater and a built-in closed helium cryostat.²³ Pressure was determined from the ratio, load/area, and it was corrected for the friction. This correction was determined during increasing pressure in a separate, *in situ* experiment using the pressure dependence of the resistance of a manganin wire. The temperature was measured by a chromel-alumel thermocouple, which had been calibrated to within ± 0.2 K against a commercially available silicon diode thermometer.

In each measurement of κ and ρC_p , the Ni-wire (hot-wire) was subjected to a 1.4 s duration heat-pulse of nominally constant power, and its electrical resistance was measured as a function of time. Subsequently, the temperature rise of the wire was calculated by using the relation between its resistance and temperature. That is, the wire acted as both heater and sensor for the temperature rise. The analytical solution for the temperature rise with time was fitted to the data points for the hot-wire temperature rise with κ and ρC_p as fitting parameters.

The hot-wire method is well-suited to establish the glass transition behaviour under pressure as the quantity ρC_p shows the typical sigmoid-shaped increase of the heat capacity C_p and the temperature dependence of κ , often decreases at the glass transition. Moreover, due to the time-dependence of the properties in the T -range that overlaps the liquid-glass-liquid transition range,

high κ and ρC_p show auxiliary features.^{24,25,26,27} We use T_{vit} for the onset temperature of liquid to glass transition on cooling, and T_g as the onset temperature of glass to liquid transition on heating.

III. RESULTS

By using our experience on crystallization of glycerol¹⁸ as a guide, we first performed experiments by temperature cycling its liquid from 298 K to a T between 100-140 K at a fixed p chosen in the range 0.1 MPa to 0.7 GPa. The results obtained are provided in Figs 1 and 2, which shows the temperature dependence of its κ and ρC_p and their respective features in the T range covering the liquid-glass-liquid transition. As before,¹⁸ at $p < 0.3$ GPa, the liquid vitrified on cooling from 298 K. However, at $p > 0.3$ GPa the liquid crystallized on cooling from 298 K. (The details of the crystallization behavior and results for the crystal phase were reported recently,¹⁸ and are therefore not given here.) To study the properties of the supercooled ultraviscous glycerol and to form its glassy state during cooling at a high p , we, therefore, avoided crystallization by the following procedure. We first cooled the liquid from ~ 298 K at 0.1 GPa to its highly viscous state, then increased p to a chosen fixed value while maintaining the liquid state. In the last step, we cooled the liquid at that fixed p to the T range of 100-140 K to form glass. (Results in the low viscosity state at $p > 0.1$ GPa, therefore, seem less relevant and they are partly excluded from the plots in Figs. 1 and 2.) Thus, we brought the liquid state to a set of eight pressures of 0.1 MPa and 0.05, 0.1, 0.3 GPa at 298 K, and 0.2, 0.4, 0.5, and 0.7 GPa at $T < 298$ K. The liquid at each of the eight conditions of fixed p was then cooled at initially 0.3-0.5 K/min rate to 100-140 K, and the sample became glass, and we measured κ and ρC_p of the sample during this cooling. The seven plots obtained at these pressures, termed as p_{cool} , are shown in Fig. 1. (The data at ambient pressure of 0.1 MPa showed a sudden small decrease, which was caused by the loss of the thermal contact of the hot wire with the glassy sample at low T , and we excluded those data.) Since the cooling under

each of the fixed p_{cool} produced a different glass of different ρ , our procedure produced seven glasses of different properties at ~ 110 K. The plots in Fig. 1 also show that $(d\kappa/dT)_p$ of the glass remains weakly positive. Unfortunately, the ρC_p values in Fig. 2 show scatter of a few percent. This is too large an uncertainty to allow one to estimate how ρC_p changes with change in p .

To ascertain the occurrence of liquid-glass-liquid transition, the glass formed by cooling under 0.1 GPa was heated under the same pressure of 0.1 GPa back to 230 K. The plot of κ obtained on heating is shown by continuous line without the data points in Fig. 1. A comparison of the κ values measured under $p = 0.1$ GPa during cooling and then heating in the 170 - 230 K shows thermal hysteresis,²⁸ and the κ values agree to within 0.9% with those obtained in the previous study.¹⁸

To study glasses formed under high p , we cooled the liquid under 0.3, 0.5 or 0.7 GPa pressure, to T below 160 K, and then decreased the pressure to 0.1 GPa during which T gradually decreased, as seen in Fig. 3. The decrease in both p and T caused κ of the glass to decrease. We then heated the glass under a fixed p of 0.1 GPa from the lowest T to ~ 298 K at initially 0.3 K/min rate. This rate gradually decreased and reached 0.2 K/min in the glass-liquid transition range. A sample that had been vitrified by cooling under the pressure of 0.1 GPa was also studied by heating back to its liquid state under the same p of 0.1 GPa. (In its qualitative effects, this procedure is similar to the usual procedure of cooling a liquid to form glass at ambient pressure and then heating the glass at ambient pressure.) The results obtained are shown in Fig. 3.

In our previous study,^{18,29} we had reported that the κ - T plots show two auxiliary peaks, labelled A and B which appear in the T range of the liquid to glass transition on cooling. The peaks appear because of the time-dependence of the heat capacity, C_p , in the temperature range of gradual freezing and unfreezing of density and structure fluctuations in the liquid-glass-liquid transition

age, which is not taken into account in our analysis,¹⁸ as elaborated in Ref. 26. These peaks too show the characteristic thermal hysteresis of kinetic freezing on cooling and unfreezing on heating,²⁸ and both the κ -peaks and a dip in ρC_p have been reported in our previous studies^{18,30,31,32,33} and those of others.^{24,29, 34}

In measurements performed by static techniques, a κ -peak does not appear. Instead, a slope inversion occurs at the liquid to glass transition temperature.^{19,35} To indicate it, we extrapolated a straight line from ~ 220 K in the plot labelled 0.05 GPa in Fig. 1, illustrating the change in slope at ~ 188 K. We find that for time scale of ~ 0.5 K/min cooling and heating the low-temperature onset T of the κ -peak labeled A appears at T close to T_m and to T_g . We will discuss their significance in terms of relaxation processes elsewhere. In summary, the appearance of κ -peak and of dip in ρC_p does not affect our discussion of the sub- T_g effects of pressure-densified glycerol, on which we now put our focus. Also, the results obtained at p of 0.05 GPa, and lower, have occasionally shown indications of loss of thermal contact between the hot-wire probe and the sample. Therefore, we use the low pressure of 0.1 GPa for studying the sub- T_g effect.

IV. DISCUSSION

A. Effect of pressure on the entropy, κ and ρC_p and their T -dependence

An increase in p generally decreases the entropy, S , increases the density, the viscosity and the relaxation time, and changes the hydrogen-bond equilibrium and the vibrational frequencies.

The change in the entropy is given by,

$$(\partial S / \partial p)_T = -\alpha V_m, \text{ or } \Delta_p S = -\alpha V_m \Delta p, \quad (1)$$

where α is isobaric thermal expansion coefficient, $\Delta_p S$ refers to the change in S on increase in the pressure by an amount Δp , and it is always negative. In statistical mechanical terms, $\Delta_p S = \Delta_p S_{conf}$

$\Delta_p S_{vib}$. Increase in density on increasing p decreases Ω , the number of available configurations.

Since $\Delta S = R \Delta \ln \Omega$, where R is the gas constant, the pressure-induced decrease in the entropy at a fixed T is given by, $\Delta_p S = R \Delta \ln \Omega_{conf} + R \Delta \ln \Omega_{vib}$. This may be interpreted to infer that increase in p decreases both Ω_{conf} and Ω_{vib} . The C_p data under high p may be used to estimate $\Delta_p S$, but such data are difficult to obtain because doing so requires C_p measurements at a fixed high p from T near 0 K to a temperature of the melt state and the entropy of melting at that high p . (The C_p data for the glass and liquid states of 1-propanol and 3-methylpentane at high pressure were reported by Takahara *et al.*³⁶ who used the data to determine the difference between $\Delta_p S$ at two temperatures. This may be done also here, but only after correcting for the dip in the ρC_p plot.) Since the changes in ρ on cooling at a fixed p is relatively small, the ρC_p plots shown in Fig. 2 follow the changes in C_p , which is significant because measurements on cooling a liquid at high p and thus of higher ρ have been rarely performed. In an interpretation in terms of $\Delta T S$, seen as the negative slope of $\kappa-T$ plots in Fig. 1 would be related to the effect on a liquid's vibration property from decreasing number of configurations available to a liquid's structure, and the slightly positive or zero slope of its glass related to variation of its vibration properties for a fixed configurational state. In Fig. 2, the large decrease in ρC_p on cooling is thus a consequence of configurational freezing of glycerol on the time scale of 0.3 s and ultimate vitrification on further cooling.

We now consider the difference between the κ of glass formed by cooling a liquid at high p relative to that formed by cooling a liquid at low p . A glass formed by cooling at a higher p is denser and its frozen-in configurational entropy is lower than those of a glass formed by cooling at a low p . A comparison of the plots in Fig. 1 shows that κ of the glassy state is higher when the glass is formed by cooling the liquid (of higher ρ) at a high p than when a glass is formed by cooling the liquid at low p and the glass density is lower. For example at 150 K, the lowest temperature for the

glass at 0.7 GPa in Fig. 1, κ of the glass is $0.429 \text{ W m}^{-1} \text{ K}^{-1}$ and $0.358 \text{ W m}^{-1} \text{ K}^{-1}$ at 0.1 GPa. We

have plotted these and intermediate pressure values for κ of glassy glycerol κ of the glass formed on isobaric cooling the liquid at different pressures in Fig. 4, shown by diamonds. The values show the κ against p plot at 150 K of glycerol glasses of different configurations and density. At $T \leq 150 \text{ K}$, κ of the glycerol glass does not greatly depend upon T , as evident in Fig. 1, therefore in Fig. 4, the plot of diamond data points would also be a plot for $T \leq 150 \text{ K}$. The results suggest that when the frozen-in configurational entropy is lower and density higher, κ of the glass is higher, *i.e.*, the phonon propagation properties depend upon the magnitude of frozen-in thermodynamic properties on glass formation.

We also investigate the effect of pressure on κ of glycerol glass of one fixed configuration obtained by cooling the liquid under a fixed p . The positive slope part of the plot labeled 3 in Fig. 3 provides the relevant data. We use these to determine how κ of the glass formed at 0.7 GPa decreases when the glass at 150 K, more than 50 K below its T_g , was depressurized, or its p decreased in a controlled manner, from 0.7 GPa to 0.1 GPa while its T was also concurrently decreased from 147 K to 116 K. As in all experiments performed on increasing or decreasing p or T here, we had measured simultaneously κ , p and T also for curve 3 in Fig. 3. Therefore each κ value on the positive slope part of the plot labeled 3 in Fig. 3 is for a different T and different p . In Fig. 4, we have plotted κ of the glass (of fixed configuration) against p , as triangles, and here each κ value is for a different $T < 147 \text{ K}$. As noted here before, κ of glycerol glass at fixed p does not change significantly with change in T when $T < 150 \text{ K}$, *i.e.*, $(d\kappa/dT)_p = 0$ for the glass at $T \leq 150 \text{ K}$. So, we neglect the T -dependence of κ of the glass in the 147 K to 116 K range and regard the plot of the data shown by triangles in Fig. 4 as a plot for κ of the glass at constant T of 150 K. Since

glycerol under these conditions is in the glassy state, the decrease in its κ with decrease in p shows the effect of changing vibrational state of a fixed configuration state.

In the plots of κ of glass against p in Fig. 4, the κ_{exc} is used to indicate the difference between κ of the isobarically vitrified glasses (diamond data) and κ of one glass formed by cooling at 0.7 GPa and then depressurizing (triangles data). The magnitude of κ_{exc} represents the combined effect of changing configurational state and the concurrent, consequential change in the vibrational state on the κ value of glycerol glass at decreasing pressure. The difference is zero at 0.7 GPa because both glasses have identical configurational and vibrational states as these are vitrified at the same conditions (at 0.7 GPa). The relatively large κ_{exc} at 0.1 GPa, shows that the higher vibrational and configurational entropy of a glass formed by cooling a liquid at low p of 0.1 GPa produce a glass of lower κ at 0.1 GPa pressure, than the lower vibration and configuration (?) entropy of a glass formed at high p of 0.7 GPa, and brought to 0.1 GPa pressure below T_{vit} . It also follows that a high-entropy, low-density state of a glass formed by vitrification at low pressure, and thereafter pressurized to high p at T well below T_{vit} , would show lower κ than a low-entropy, high-density glass formed by vitrification at that high- p .

As mentioned earlier here, a glass formed by cooling under high p has a higher density when measured at that high p and a lower C_p , enthalpy and entropy, than a glass formed by cooling under low p when measured at that low p . A glass formed under high p also has a higher κ at that high p , as is seen in Fig. 1 here. This also suggests that configurational state of a glass has an effect on its κ , and there is a qualitative relation between the kinetically frozen thermodynamic quantities and κ . But the present theories of κ of solids do not seem to yield a quantitative relation between these quantities and κ .

Thermal conductivity of ordered crystals is the same whether it is measured on heating or cooling, pressurizing or depressurizing, and it does not depend upon the time taken to measure it. It is interpreted in terms of the Debye equation,

$$\kappa_{\text{crystal}} = 1/3 \rho C v^2 \tau_s = 1/3 \rho C v l, \quad (2)$$

where v is the phonon propagation velocity, τ_s is the time between two (phonon) scattering events, and l is the phonon mean free path. Equation (2) is used for glasses also, with the provision that the mean free path ($l = v\tau_s$) in the glass varies with T differently from that in the crystal state. For a glass at T far below the glass-liquid transition range, κ_{glass} and its features are also reversible.

Figure 3 shows the results obtained on slow cooling while p was simultaneously decreased at a T well below T_{vit} . At such low T , the configurational state does not change with decrease in p , and the weak temperature variation of κ_{glass} in Fig. 1 shows that κ_{glass} does not decrease because of the T decrease by ~ 25 K. Thus, the change in κ_{glass} seen in Fig. 3 during slow cooling and depressurization is due entirely to decrease in p . Since the change is due entirely to the change in the vibrational state of the glass, we refer to it as $\Delta_{\text{vib}}\kappa$ and interpret it in terms of Eq. (2), i. e., $\kappa_{\text{glass}} = 1/3 \rho_{\text{glass}} C_{\text{glass}} v_{\text{glass}} l_{\text{glass}}$, and we stress that this model for $\Delta_{\text{vib}}\kappa$ is based on the properties of a fixed configuration, which in turn depend upon the conditions of glass formation.

The pressure derivative of the fractional change in κ_{glass} with p at a fixed T may be written as,

$$\left(\frac{d \ln \kappa_{\text{glass}}}{dp} \right)_T = \left(\frac{d \ln \rho_{\text{glass}}}{dp} \right)_T + \left(\frac{d \ln C_{\text{glass}}}{dp} \right)_T + \left(\frac{d \ln v_{\text{glass}}}{dp} \right)_T + \left(\frac{d \ln l_{\text{glass}}}{dp} \right)_T \quad (3)$$

where the change in phonon velocity can be rewritten in terms of the Debye-Grüneisen parameter γ ,

$$\gamma = \frac{1}{3} + \left(\frac{d \ln v_{\text{glass}}}{d \ln \rho} \right)_T \quad (4)$$

Since C_p of a glass at high p is found to be slightly less than at low p ,³⁶ a higher κ_{glass} would be mainly due to a higher ρ_{glass} , and the consequential increase of phonon velocity. Neglecting the changes in C_{glass} , and assuming that l_{glass} is proportional to the intermolecular distance, i.e. $l_{\text{glass}} \sim \rho_{\text{glass}}^{-1/3}$, yields,

$$\left(\frac{d \ln \kappa_{\text{glass}}}{dp} \right)_T \cong \left(\gamma + \frac{1}{3} \right) \left(\frac{d \ln \rho_{\text{glass}}}{dp} \right)_T, \text{ or } \left(\frac{d \ln \kappa_{\text{glass}}}{dp} \right)_T \cong \left(\gamma + \frac{1}{3} \right) \beta_{\text{glass}} \quad (5)$$

where $\beta_{\text{glass}} = (1/\rho)(d\rho/dp)_T$ is the isothermal compressibility of a glass of fixed configuration.

Equation (5) implies that the fractional change in κ_{glass} with p is proportional to the compressibility.

It also implies that the density dependence of κ_{glass} , i.e. the Bridgman parameter: $(d \ln \kappa_{\text{glass}}/d \ln \rho)_T = \gamma + (1/3)$, is a constant unless the effect of anharmonicity, measured in terms of the Gruneisen parameter, γ , changes with pressure. In the case of glassy glycerol, and for most other glasses, its value is positive since γ of glassy glycerol is positive. Thus, κ_{glass} increases with increase in p even though C decreases slightly. If a glass formed by cooling a liquid at high p was allowed to expand by decreasing p at a fixed T well below T_{vit} , in a similar manner as the glass for which the results in Fig. 4 (triangles) are given, then the expansion on depressurizing would be elastic and it can be reversed by increasing p . Only then it may be written in terms of β or the bulk modulus of the glass.

The configuration of a liquid has an associated vibrational state, and the two change together with T and p . When a glass forms, a configurational property becomes fixed and the vibration property changes on change in T and p . Analogous to the usual discussion of a property, we may also discuss $\kappa_{\text{glass}}(p)$ of such glasses (Fig. 1) in terms of Eq. (5), assuming that γ of glasses varies weakly with their preparation condition. In that case, β_{glass} would be the compressibility derived from the volume of glasses formed by isobaric cooling at different p and, therefore, different from that of an isothermally pressurized or depressurized glass. It is known that the mean free path in a

disordered structure and β_{glass} , C_{glass} , and v_{glass} all vary with the structural disorder. If the differences in configurational state of a glass formed by different T and p paths were to be small, this difference would also be small and Eq. (5) can be used with the provision that β_{glass} is derived from the volume of isobarically vitrified glasses.

B. Instability of a depressurized, high-density glass

As mentioned earlier here, one can observe the additional instability of a pressure-densified glass at a low p by measuring κ during heating at a fixed rate in a short-period experiment, even though the results obtained contains the effect of increasing T . The measured κ for the three glasses formed by freezing at 0.7, 0.5 and 0.3 GPa, respectively, are shown in Fig. 3. As a glass formed at high p is unstable at low p , its heating at low p causes a gradual change in the configurational state. This decreases κ_{exc} , which is detected as a gradual decrease in κ of the glass in Fig. 3. On heating at 0.1 GPa this decrease in κ of the glass begins at ~ 160 K for the 0.7 GPa glass, and at T slightly above 170 K for the 0.3 and 0.5 GPa glasses. In Fig. 3, κ_{exc} for all glasses at a fixed p of 0.1 GPa decreases on heating by 50 % at $188 \text{ K} \pm 1 \text{ K}$. From the known change of the relaxation time at the κ -peak,²⁶ we estimate that T_{vit} on isobaric cooling at 0.1 GPa, is higher than, or about, 192 K. That is, the instability of the high-pressure glasses is observed well below T_{vit} .

Calorimetric studies of glasses formed under high p and studied at ambient- p , as reviewed in Refs. 12, 13 and 14, have shown that features of C_p and volume observed on heating of high- p formed glasses at ambient- p are distinguished from the corresponding features of glasses formed at ambient- p and heated at ambient- p . Generally speaking, when a glass formed at a high p is heated at a low p and its state approaches the equilibrium metastable liquid state at that low p , the following two irreversible processes would occur: (i) ρ would decrease as the vibrational frequencies decrease, and (ii) ρ would *increase* towards the equilibrium liquid value. Process (i) occurs only in

the depressurized state of the glasses formed at high p , and process (ii) occurs in the glasses formed and kept at the same p . Initially process (i) dominates and ultimately process (ii) dominates. The two processes compete so that the net effect during heating would be the result of their combined occurrence. Only process (i) is characteristic of the sub- T_g effects observed for glasses formed under high p and studied at a low p . Only process (ii) is characteristic of glasses formed and studied at the same p . None of the two processes occur in the equilibrium state.

A glass formed at high p is in an internal pressure at a low p . One experimentally testable prediction of this internal pressure is that if such a glass is kept immersed isothermally in an inert liquid at ambient- p , its relaxation to a low-density state would increase the pressure on the liquid. This may be determined either by measuring the increase in p in a sealed container, or more conveniently by measuring the rise in the level of the liquid in an open capillary attached to the liquid-filled container. As the glass expands, by process (i) the rate of expansion would decrease isothermally, as for a kinetic process generally. If process (i) and (ii) are well-separated in time, then after a certain time period, expansion by process (i) would become unobservable as the glass internal pressure plus its surface tension approach those of the liquid. After that, it would begin to contract by process (ii) until its equilibrium state of high-density is reached. The level of the liquid in the capillary would first increase with time to a certain height and then would begin to decrease until it reaches a constant value. A glass formed at ambient p would only show a decrease in the liquid level in the capillary.

It is known that κ of the glass generally increases reversibly when its ρ is increased by pressurizing, and decreases reversibly when its ρ is decreased by depressurizing. In contrast, the decrease in κ of the glass in Fig. 3 observed here on heating at 0.1 GPa the glasses that had been formed by cooling the liquid at 0.3, 0.5 and 0.7 GPa indicates the irreversible effects of decrease in ρ on stabilization of the *glass structure to its true ρ value* at that low p . The effect is *opposite* to

ing of physical aging which increases ρ and would increase κ of the glass, as indicated by the arrow in the inset of Fig. 2 in Ref. 18, and shown by Hiki *et al.*³⁷ in a study of κ of AgI-AgPO₃ during isothermal physical aging at $T < T_g$.

One reviewer of this paper asserted that we compare the kinetically more *unstable* high-pressure formed, high-density glasses at 0.1 MPa pressure against the vapor-deposited, kinetically *ultrastable* high-density amorphous solids (HD-VDAS) at 0.1 MPa pressure, which have come to be regarded as glasses.³⁸ The HD-VDAS state of a large variety of materials has now been prepared and their properties have been studied. A review by Ishii and Nakayama³⁹ and citations numbered 1-30 in Chua *et al.*'s paper⁴⁰ indicate the wide-spread interest in this subject. One may argue that (HD-VDAS) do not inherit one of the structures of the melt and therefore, they should not, strictly speaking, be considered as glasses. It is uncertain how to relate them to the structure of a glass even when they are described as a low fictive temperature state.⁴¹

The high kinetic stability of HD-VDAS has been attributed to the layer-by-layer formation of the disordered structure and an enhanced mobility of surface molecules, which is believed to allow these solids to find a low-energy high density state even when the substrate is kept at T well-below T_g . In contrast to glasses, HD-VDAS show a growth front transformation mechanism and birefringence. In practical use of these results, high thermal stability of a *glass* has been associated with brittleness whereas the low stability of high-pressure produced *glass* has been associated with higher ductility.¹⁷ In view of the rapidly evolving knowledge on the apparently distinct state of HD-VDAS, it seems prudent to postpone further discussion of their *higher* kinetic stability *vis-a-vis* *lower* kinetic stability of the high-pressure formed glasses at ambient pressure.

CONCLUSIONS

- (1). A glass formed by cooling the liquid at high p is additionally unstable when kept at a low p . This instability, which differs from the usual instability of a glass, is less when the difference between the two pressures is less and it too is due to the incompatibility of the vibrational state with the configurational state, which may also involve, as in all hydrogen-bonded liquids, the non-equilibrium population of hydrogen bonds in glycerol.
- (2). The manner in which κ changes on heating a high- p formed, high-density glycerol glass is different from the manner in which κ changes on heating a usually formed glycerol glass. The change in κ when a pressure-densified glass is heated at a low p is determined by two competing processes. The first process tends to decrease it and the second process tends to increase it. The first process starts at T well below the T_g of a normally formed glass or of a glass formed by cooling at a low- p . The second process has also been observed as an increase in κ of a glass formed at ambient p and kept isothermally at ambient p .³⁷ The first of these processes decreases the density and increase the entropy as the vibrational and configurational states of the glass mutually approach the same state at its low- p , and the second process increases the density and decreases the entropy as a glass formed at a given p is heated at the same p and approaches the high- density, low-entropy state of its metastable liquid at that p . The effect should be present in ρC_p but this effect is too small to be observed here, probably due to partial cancellation of the opposite changes occurring in ρ and C_p .
- (3). Thermal conductivity of a pressure-densified glass is higher when its density is higher and the frozen-in configurational entropy is lower. This may be attributed to the effect of increase of density and decrease in the frozen-in configurational entropy on the phonon propagation features. Thermal conductivity of a given pressure-densified glass of fixed frozen-in configurational entropy decreases when the pressure on the glass is decreased, which is attributed to the effect of pressure on phonon propagation features.

An interesting aspect of pressure-destabilized glasses is worth investigating in the future as follows: If a glass is formed by cooling at ambient- p is pressurized at a low T to a pressure p and then heated, its κ would increase slowly as its structure densifies at a progressively faster rate and then will show a change in $(d\kappa/dT)_p$ at a higher T corresponding to the T_g at that high p .

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- ²⁶ A peak in κ and dip in ρC_p appear because of a time-dependence in C_p due to the kinetic unfreezing of structural fluctuations in the glass to liquid transition range, which is not accounted for here because κ and ρC_p are treated as adjustable, *time-independent*, parameters in the fitting of the analytical solution for the temperature rise of the hot-wire. The effect is most pronounced when the C_p change occurs during the probing time of 1.4 s (see experimental section). This feature has been previously analyzed in detail (Ref. 25) and it was found that the peak maximum in these experiments occurs at a relaxation time of about 0.3 s. (It is ~ 0.01 s at the beginning of the peak at the high T end and ~ 100 s at the end of the peak at the low T end.) The peak is thus superimposed on the real changes in κ due to the change in T and due to the inversion of the slope of κ at vitrification. In addition to the experimental time-scale set by the transient heating of the hot-wire probe, with an average heating rate of 150 K/min (3.5 K in 1.4 s), there is another time-scale determined by the slow heating and cooling rates of the vessel of less than 1 K/min. A cooling rate of 0.3-0.5 K/min used in the studies here typically leads to vitrification when the α -relaxation time ~ 100 s, which means that the sample vitrifies at near the low- T end of the low-temperature peak.

(The relatively slow cooling and heating of the pressure vessel, with a rate of less than 1 K/min, is superimposed on the rapid heating of the probe and does not cause the sample to kinetically freeze or unfreeze during the heat pulse.)

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Figure Captions

FIG. 1. Thermal conductivity of glycerol measured on cooling at the indicated pressures is plotted against the temperature. One set of data obtained on heating at 0.1 GPa (red continuous line) show the thermal hysteresis of the peak features. The peaks labeled “A” and “B” are two artificial peaks in κ , which arise due to two distinct relaxation processes. The black solid line below the two peaks at 0.05 GPa indicates the true $\kappa(T)$ of the liquid. The data at 0.2 GPa are taken from Ref. 18.

FIG. 2. Heat capacity per unit volume of glycerol measured on cooling at the indicated pressures is plotted against the temperature. The inset shows an expanded plot of the glass transition range at 0.1 GPa. The data for ρC_p at 0.5 GPa contained the effect of partial crystallization and therefore these data are excluded.

FIG. 3. Thermal conductivity of glycerol measured on heating at initially 0.3 K/min rate at 0.1 GPa is plotted against the temperature. This rate gradually decreased and became 0.2 K/min in the region of the κ peaks, which is the temperature range of glass-liquid transition before crystallization began at about 235 K. The samples (labelled 1-3) had been vitrified at 0.3 GPa (1), 0.5 GPa (2) and 0.7 GPa (3), as indicated for each data set, and then the glasses were depressurized to 0.1 GPa while the temperature and κ decreased. These data are also shown and marked by arrows pointing left and down.

FIG. 4. Thermal conductivity of glycerol glass is plotted against the pressure: Triangles denote the values measured on controlled depressurization of glycerol glass from 0.7 GPa to 0.1 GPa at $T < 147$ K, in the plot of positive slope which is part of curve 3 in Fig. 3. Diamonds denote the values at 150 K measured on isobaric cooling from the liquid at different p , as shown in Fig. 1, and each data

corresponding to this p . The vertical difference is κ_{exc} of a glass of fixed configuration in excess of that for the glass vitrified and studied by isobaric cooling of the liquid at different p . At $T \leq 150$ K, κ of glycerol glass does not significantly depend upon T , therefore both plots would also be plots for T at 150 K.