Electronic Supplementary Information

Elastic properties of the hydrogen-bonded liquid and glassy glycerol under high pressure: Comparison with propylene carbonate

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1. The homogeneous isotropic medium approximation

In order to calculate the shear G and bulk B elastic moduli from ultrasonic measurements, we used the homogeneous isotropic medium approximation:

$$G = \rho v_t^2, \tag{1}$$

$$B + \frac{4}{3} G = \rho v_l^2, \tag{2}$$

where ρ is the density, and v_t and v_l are the transverse and longitudinal ultrasonic velocities, respectively. The Poisson's ratio was calculated in the same approximation by the formula

$$\sigma = \frac{3B - 2G}{6B + 2G}. \tag{3}$$

2. Elastic moduli of supercooled liquids

Special attention should be paid to ultrasonic measurements of elastic moduli in supercooled liquids, particularly, in glycerol [1-4]. In general, there are three contributions to the bulk or shear moduli of a condensed matter: low-frequency part, frequency-dependent relaxation term, and imaginary part corresponding to attenuation [1, 2]. In a liquid state, the static (low-frequency) shear modulus is equal to zero, and the low-frequency compressional modulus of the liquid becomes equal to the static bulk modulus. As the compressional modulus, we mean the value $B^* + (4/3)G^*$ defining velocity and attenuation of longitudinal wave (here, the asterisk denotes summation of all three parts mentioned above).

In our measurements of sound velocities, we deal with the low-frequency limit for two reasons. First, we cannot detect a steady signal in pressure-temperature regions with a significant attenuation due to specific constructive features of the high-pressure ultrasonic piezometer, and corresponding fragments of experimental curves are omitted in corresponding figures. Second, the previous careful frequency-dependent study of glycerol [1-4] shows that our working frequencies of 5 and 10 MHz can be considered as belonging to the low-frequency limit for both liquid and glassy glycerol at those temperatures where we measure ultrasonic velocities.

3. Relation between isothermal and adiabatic bulk moduli

Ultrasonic measurements at megahertz frequencies provide experimental data for adiabatic elastic properties. The relation between the isothermal bulk modulus B_T and adiabatic modulus B_S is determined by the equation [5]

$$\frac{B_S}{B_T} = 1 + \frac{\alpha^2 T B_S}{\rho c_P} = 1 + \alpha \chi T,$$
(4)

where α is the volume thermal expansion coefficient, c_P is the specific heat at constant pressure, ρ is the density of a substance, and χ is the Grüneisen parameter, which is of the order of 1–2 for usual condensed phases. From the tabular data and the middle part of eqn (4), the difference between B_T and B_S at room temperature is equal to ≈22% for liquid PC and to ≈14% for liquid glycerol, and is relatively large due to the large values of the volume thermal expansion coefficients [6, 7]. If we fix the Grüneisen parameter obtained at atmospheric pressure from eqn (4), we can calculate the pressure dependence of B_S/B_T from the data on the volume thermal expansion of glycerol and PC under pressure, obtained by digitizing Figs. 2 and 4 in Ref. 7.

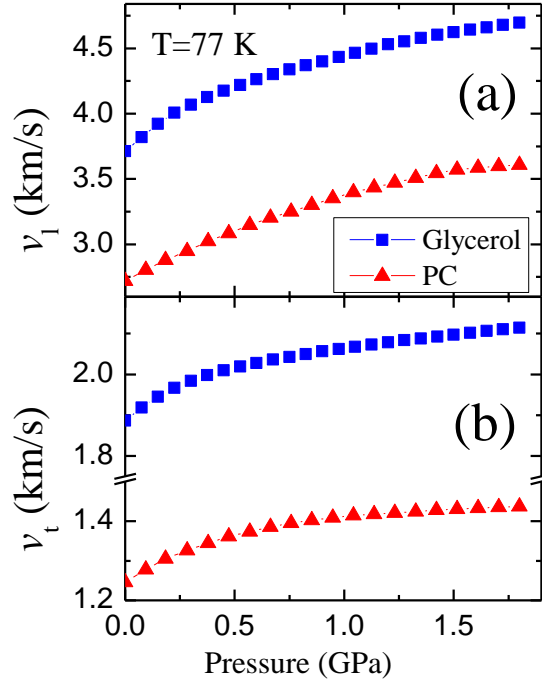## 4. Pressure dependences of ultrasonic velocities at 77 K

Fig. 1S Pressure dependences of the (a) longitudinal and (b) transverse wave velocities for glassy

glycerol and propylene carbonate at liquid nitrogen temperature.

5. Poisson's ratio in substances with central interparticle forces

If the lattice structure is such that every lattice particle occupies a center of symmetry and if the particles interact with central forces, then the Cauchy relations are fulfilled for elastic constants [8], particularly, $c_{23}=c_{44}$, $c_{31}=c_{55}$, and $c_{12}=c_{66}$. For isotropic polycrystalline state in the Voigt approximation [9], we obtain for bulk and shear polycrystalline moduli:

$$9B_V = (c_{11}+c_{22}+c_{33})+2(c_{44}+c_{55}+c_{66}), \tag{5}$$

$$15G_V = (c_{11}+c_{22}+c_{33})+2(c_{44}+c_{55}+c_{66}), \tag{6}$$

This means $9B_V = 15G_V$, and Poisson's ratio $\sigma = 0.25$. In the Reuss approximation [9], Poisson's ratio is usually higher than 0.25 by several percent for majority of substances. For isotropic substance with the Cauchy relation ($c_{12}=c_{44}$) the additional equality, $c_{11}-c_{12}=2c_{44}$ [10], leads to the exact relation $\sigma = 0.25$, because of both Voigt and Reuss approximations as extremes for B and G [9] give 0.25 for Poisson's ratio.

Taking into account that the strong O–H···O hydrogen bonds are directional with the O–H–O angle close to 180° (more exactly, between 160° and 180°) [11, 12], and the contribution of

hydrogen bonds is well described by the pair central forces in the empirical potentials [13-15], one can conclude that the relation between Poisson's ratios for glycerol and PC with respect to 0.25 is evidence of the hydrogen bonding in glycerol.

6. Correlation between Poisson's ratio σ and isobaric fragility

At atmospheric pressure, it is known the correlation between Poisson's ratio σ and isobaric fragility m_P. The last characteristic is introduced as a quantitative measure of the degree of departure from the Arrhenius behavior in a supercooled liquid[16-19] and is considered as a pressure-dependent parameter[20-22]. This correlation is described for non-metallic glass formers in terms of the B_∞/G_∞ ratio by the formula [23, 24],

$$m_P = (29 \pm 2)\frac{B_\infty}{G_\infty} - (12 \pm 5), \tag{7}$$

where B_∞ and G_∞ are limiting high-frequency bulk and shear elastic moduli. Here, we can use the B/G ratio at 77 K as a good approximation for the B_∞/G_∞ ratio.

Taking interpolations for the $m_P(P)$ dependence for glycerol[25, 26] and PC[27] (these papers also cite previous studies of $m_P(P)$) and using eqn (3) and (7), one can found in Fig. 2S the areas of possible σ values following from correlation between σ (or B/G ratio) and $m_P(P)$. The corresponding middle curves are also shown in Fig. 2S. Interplay between experimental $\sigma_{\exp}(P)$ and $\sigma(m_P(P))$ dependences for PC have been discussed in detail previously.[27] Here, we briefly compare glycerol and PC, highlighting common features and difference between them. At atmospheric pressure correlation between $\sigma_{\exp}$ and $\sigma(m_P)$ for glycerol is worse than that for PC (Fig. 2S), but $\sigma_{\exp}$ is within the uncertainty of eqn (7). The $m_P(P)$ dependence for glycerol has a positive slope,[25, 26] while this slope for PC is negative[27] as for ordinary liquids.[18] Automatically, the slopes of the correlation curves $\sigma(m_P(P))$ are also opposite for glycerol and PC. At the same time, $\sigma_{\exp}$ increases in both glasses. The general trend observed with increasing pressure is that the $\sigma_{\exp}(P)$ and $\sigma(m_P(P))$ dependences for both glassy glycerol and PC differ from each other almost identically. Summarizing, the correlation between Poison's ratio σ (or B/G ratio) and isobaric fragility m_P ceases to be observed under pressure for glasses with and without strong hydrogen bond.
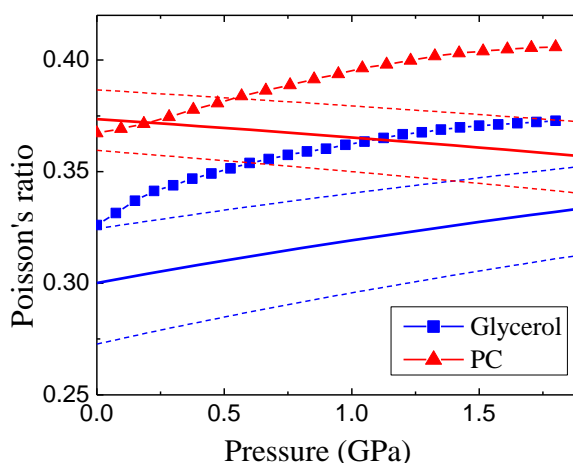
Fig. 2S Pressure dependences of the experimental Poisson's ratios (line with symbols) for glassy glycerol and propylene carbonate at liquid nitrogen temperature. Estimates of Poisson's ratio $\sigma(m_P(P))$ from the approximated pressure dependence of fragility according to eqn (7) are shown as solid lines (eqn (7) without deviation of the coefficients). Dashed lines show the boundaries of the possible approximated values $\sigma(m_P(P))$ (eqn (7) with the maximum deviation of the coefficients in both directions).

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