

Electronic Supplementary Information

Elastic properties of liquid and glassy propane-based alcohols under high pressure: The increasing role of hydrogen bonds in a homologous family

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S1. Calculation of density and elastic moduli

Using the definition of the isothermal bulk modulus, $B_T = -V \left(\frac{dP}{dV} \right)_T = \rho \left(\frac{dP}{d\rho} \right)_T$, where V

and ρ are volume and density, we obtain that $\left(\frac{d\rho}{dP} \right)_T = \frac{\rho}{B_T}$ and, subsequently, for pressure

dependence of density

$$\rho(P) = \rho_0 + \int_0^P \frac{\rho}{B_T} dP. \quad (1)$$

Here one can take the atmospheric value for initial density ρ_0 in the case of our pressure range.

Introducing the adiabatic (isentropic) bulk modulus B_S related to B_T by the equation,¹

$$\frac{B_S}{B_T} = 1 + \frac{\alpha_p^2 T B_S}{\rho c_p} \equiv 1 + \xi, \quad (2)$$

where α_p is the volume thermal expansion coefficient, c_p is the specific heat at constant pressure, we can calculate density from experimental ultrasonic transverse v_t and longitudinal v_l velocities as functions of pressure. In the homogeneous isotropic medium approximation^{2, 3} for shear G and adiabatic bulk B_S moduli one can use equations,

$$G = \rho v_t^2 \text{ and } B_S + \frac{4}{3}G = \rho v_l^2, \quad (3)$$

From Eqs. (1)–(3) one can obtain direct relation between density and the experimentally measured ultrasonic velocities,

$$\rho(P) = \rho_0 + \int_0^P \frac{1 + \xi}{\left(v_1^2 - \frac{4}{3} v_t^2 \right)} dP, \quad (4)$$

which is simplified for ordinary (non-viscous) liquids,

$$\rho(P) = \rho_0 + \int_0^P \frac{1 + \xi}{v_1^2} dP. \quad (5)$$

In the first approximation, we can take $\xi \approx \xi_0 = \text{const}$, where ξ_0 can be easily calculated from the atmospheric tabulated parameters (see the next section), although this issue requires separate consideration for particular substances (see Sec. 3S). Subsequently, the pressure dependences of the adiabatic elastic modulus are calculated as $B_S(P) = \rho(P)v_1^2(P)$, and $B_T(P) = B_S(P) / [1 + \xi(P)] \approx B_S(P) / (1 + \xi_0)$.

S2. Atmospheric reference data

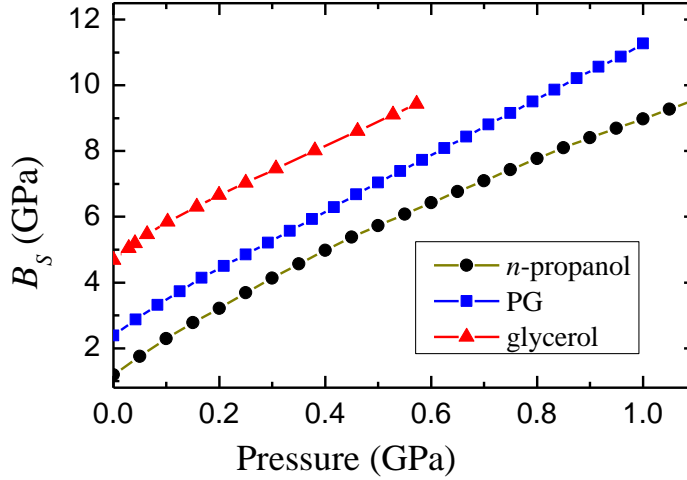
All necessary for calculation characteristics for n-propanol, propylene glycol, and glycerol in liquid states, as well as the values of the elastic moduli and their pressure derivatives, are presented in Table S1. There, comments are also given on how the quantities have been obtained. Eq. (2) was used to calculate the value of $1 + \xi_0$, but the experimental values of the ratio B_S/B_T are given for comparison, where the values of the moduli are taken from ultrasonic measurements and direct measurements of density, respectively, with the exception in Ref. ⁴. The values v_1 and dv_1/dP are given in Table S1 only for atmospheric pressure, but for the approximation of the initial part of $v_1(P)$ dependence in the case of our measurements, we considered the corresponding $v_1(P)$ data as a whole. The necessity of such approximation is due to the fact that at the initial pressures $P < 0.15$ GPa we have a sufficiently large measurement uncertainties due to friction in the piston-cylinder system and the corresponding nonlinearity of the pressure change with the load increase. In addition, this approximation solves the problem of more accurate linking of the relative distance measurements to the absolute initial length of the liquid sample in the capsule.

Table S1. The atmospheric pressure data ^{a)} (at temperature $T = 293$ K) with corresponding references for three liquids, including density ρ , longitudinal ultrasonic velocity v_1 and its pressure derivative dv_1/dP , bulk adiabatic B_S and isothermal B_T moduli and their pressure derivatives, the ratio of adiabatic and isothermal moduli B_S/B_T , isobaric coefficient of thermal expansion α_p , molar isobaric heat capacity c_p^* , specific isobaric heat capacity c_p , the ratio of adiabatic and isothermal moduli $(1 + \xi)$ from Eq. (2), and glass transition temperature T_g .

| | <i>n</i> -Propanol | Propylene glycol | Glycerol |
|--|---|--|--|
| Liquids, $T = 293$ K ^(a) | | | |
| ρ , g/cm ³ | 0.804 ⁵⁻¹⁰ | 1.036 ^{4, 11, 12} | 1.261 ^{13, 14, b)} |
| v_1 , km/s | 1.219 ¹⁵ , 1.223 ⁷ | 1.522 ⁴ | 1.907 ¹⁶ , 1.923 ¹⁷ , 1.927 ^{18, 19} |
| dv_1/dP ^{c)} , km/(s·GPa) | 5.81 ⁷ , 5.66 ²⁰ | 3.806 ⁴ | 2.1 ^{18, 19} |
| B_S ^{d)} , GPa | 1.199 ^{e)} , 1.208 ¹¹ | 2.40 ^{e)} , 2.37 ¹¹ , 2.402 ⁴ | 4.67 ^{e)} , 4.66 ¹⁶ , 4.684 ¹⁸ |
| dB_S/dP ^{c)} | 11.3 ²⁰ | 12.9 ⁴ | 10.8 ¹⁶ , 11.6 ¹⁸ |
| B_T ^{f)} , GPa | 1.033 ⁷ , 1.022 ⁹ , 1.006 ¹⁰ | 2.13 ²¹ , 2.114 ⁴ , 2.34 ²² | 4.2 ²³ , 4.477 ¹⁴ |
| dB_T/dP ^{c)} | 9.73 ⁷ , 10.7 ¹⁰ | 11.6 ⁴ , 9.4 ²² | 8.97 ¹⁴ |
| B_S/B_T ^{g)} | 1.157, 1.201 | 1.113, 1.136 | 1.041, 1.115 |
| α_p , $10^{-4} \cdot \text{K}^{-1}$ | 9.9 ^{5, 10} , 9.5 ⁹ | 7.04 ⁴ | 4.25 ^{14 h)} |
| c_p^* , J/(K·mole) | 141 ²⁴ | 187.8 ⁴ | 218 ²⁵ , 216.8 ¹⁴ |
| c_p , J/(K·g) | 2.35 ⁱ⁾ , 2.348 ⁷ | 2.47 ⁱ⁾ | 2.36 ⁱ⁾ |
| $1 + \xi_0$ | 1.183 | 1.136 | 1.083 |
| T_g , K | 96.2 ²⁶ | 168 ²⁷ | 188 ^{28, 29} |

- a) The corresponding values are taken directly from the tables, obtained by interpolation or extrapolation from closely spaced points, or calculated by digitizing graphs.
- b) Many other references on density are provided in these two papers.
- c) The derivatives are obtained by differentiation of the third or fourth order polynomial fitting the data, since, as a rule, the number of measured points is about ten.
- d) In the cited papers, adiabatic (isentropic) compressibility $k_S = 1/B_S$ is usually given.
- e) The value is calculated according to the equation $B_S = \rho v_1^2$.
- f) The values are obtained from the tabulated isothermal compressibility or by differentiating the density dependence $\rho(P)$ and using the definition, $B_T = -V(dP/dV)_T = \rho(dP/d\rho)_T$.
- g) We give the minimum and maximum possible ratios obtained from the previous values of bulk moduli.
- h) Isobaric coefficient of thermal expansion α_p is calculated by differentiation of the $\rho(T)$ dependence.
- i) Specific heat capacity c_p is calculated from the molar heat capacity c_p^* .

S3. Pressure dependences of adiabatic (isentropic) bulk moduli for three liquids at $T = 293$ K (Fig. S1)



S4. Relation between adiabatic and isothermal bulk moduli in liquids at $T = 293$ K

A special discussion on the pressure dependence of $1 + \xi$ is required in the case of liquid phases, since the difference between B_s and B_T moduli is large enough (Table S1). We could not find the values of all parameters included in Eq. (2) for glycerol and n-propanol under pressure. Fortunately, such data are available for propylene glycol at room temperature up to 0.1 GPa.⁴ The results of calculation of $1 + \xi(P)$ and approximations in a wider pressure interval are shown in Fig. 2S. We chose 3 functions (Table S2) to extrapolate the $1 + \xi(P)$ dependence along with the simplest approximation, $\xi(P) = \xi_0$. The parameters of the functions were adjusted by the least squares method on the known experimental section of the dependence. Extrapolation of the dependence to a much wider (by 10 times) pressure interval is a very inaccurate procedure. However, function 2 (Table S2) can be considered as an upper bound because of a very rapid change in the derivative $\xi'(P)$ beyond the known pressure interval of the experimental function. Function 4 can be considered as a lower estimate, since it crosses straight line $1 + \xi(P) = 1$ relatively quickly and goes to the unphysical range of the $1 + \xi$ values. Function 3 appears to be the better approximation. The calculation of density and relative volume (Fig. S3) for 4 models gives the maximum possible uncertainty $\approx 0.5\%$. The real accuracy of the determination of the density and relative volume can be estimated from comparison of the $\Delta V/V_0(P)$ curves for functions 3 and 4 (Fig. S4, A) and seems to be less than 0.25%. The same uncertainty should be

expected for the adiabatic bulk modulus, $B_S = \rho v_1^2$. Such the small variation is due to the fact that at initial pressures, when the sound velocity is relatively small, the deviation of $1 + \xi$ from the correct value is insignificant. With increasing pressure, the quantity v_1^2 in the integral of Eq. (5) rapidly increases, and the deviation of $1 + \xi$ ceases to play an appreciable role for the value of the integral. From the relationship $B_T = B_S / (1 + \xi)$, it is clear that the accuracy of determination of the isothermal bulk modulus at maximum pressure and its pressure derivative $B'_T(P)$ significantly lower, reaching 6% when comparing $B_T(P)$ dependences for functions 1 and 4 (Figs. S3 and S4, B), but rather closer to 2-3%. Comparison of our calculation of the density of propylene glycol with the recent measurement of density at pressures up to 0.35 GPa²² shows coincidence within 1% in the specified range of pressure.

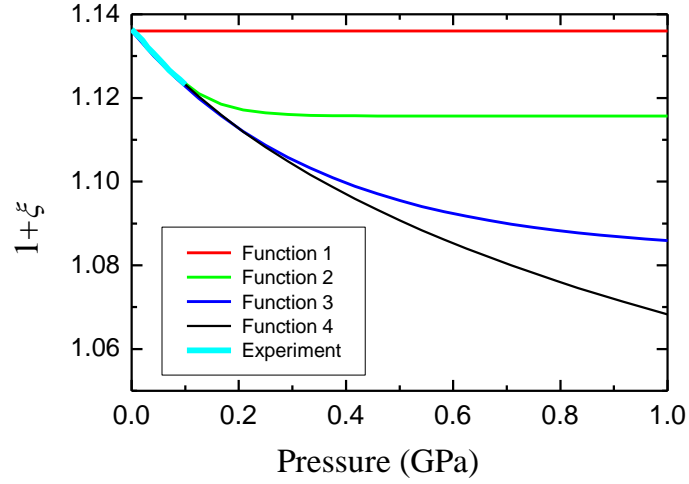


Fig. S2 Pressure dependences of the model $1 + \xi$ parameter for propylene glycol at 293 K, along with the experimental data from Ref. ⁴.

Table S2. Model functions for extrapolation (Fig. S2) of the experimental $(1 + \xi)$ vs P dependence⁴ and parameters of the best fits for the experimental points for propylene glycol at 293 K.

| N | Model function | The best fit |
|---|---|--|
| 1 | $1 + \xi = \text{const}$ | $1 + \xi_0 = 1.136$ |
| 2 | $A_2 + \frac{A_1 - A_2}{1 + \exp\left(\frac{P - P_0}{\Delta P}\right)}$ | $1.11569 + \frac{1.14931 - 1.11569}{1 + \exp\left(\frac{P - 0.02806}{0.05835}\right)}$ |
| 3 | $A_0 + A_1 \exp\left(-\frac{P}{P_0}\right)$ | $1.083 + 0.053 \exp\left(-\frac{P}{0.34594}\right)$ |
| 4 | $(A + BP)^{-\left(\frac{1}{C}\right)}$ | $(0.054 + 0.16793P)^{-\left(\frac{1}{22.79957}\right)}$ |

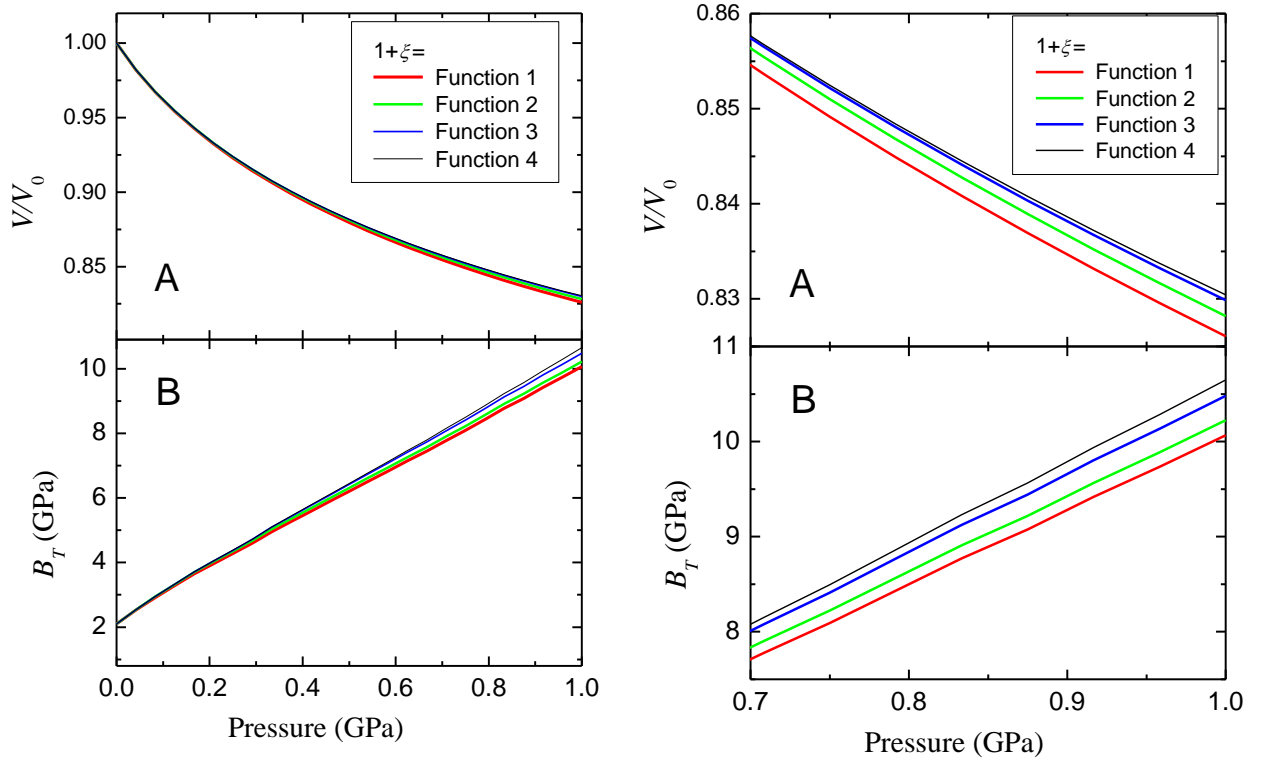


Fig. S3 Pressure dependences of the relative volume (A) and isothermal bulk modulus (B) for propylene glycol at 293 K, calculated using the different models from Table S2.

Fig. S4 High-pressure parts of the pressure dependences from Fig. S3.

In the case of glycerol, the most likely known experimental dependences of adiabatic compressibility¹⁸ and isothermal compressibility¹⁴ give the underestimated ratio, $B_S/B_T(0) = 1.041$, with respect to the thermodynamic value $1 + \zeta_0 = 1.083$, but a positive value of the derivative $d\xi/dP(0)$. The positive value of $d\xi/dP(0)$ is also confirmed by an elementary estimate from the equation:

$$\frac{d\xi}{dP} = \frac{B'_S}{B_T} - \frac{B_S B'_T}{B_T^2}. \quad (6)$$

At the same time, the value of $1 + \xi$ should begin to decrease with further increase of pressure. Therefore, for glycerol a good choice is the constant function, $1 + \xi = 1 + \xi_0$. From Eq. (6), the value of $d\xi/dP(0)$ for n-propanol is negative and larger in module than that for propylene glycol. In this case, we took function 3 from Table S2, which was scaled to obtain the initial value of $1 + \xi_0$ for n-propanol.

The accuracy of the approximation $1 + \xi(P) = 1 + \xi_0$ can be checked for methanol as example of alcohols. There is a complete set of tabulated experimental data for the liquid methanol at different temperatures up to a pressure of 0.8 GPa.³⁰ Numerical differentiation of isobaric and isothermal sections of volumetric data made it possible to calculate the coefficient of thermal expansion and the isothermal bulk modulus. The adiabatic bulk modulus was calculated from the dependences of the density and longitudinal sound velocity. First, we checked equation (2), which was performed with an accuracy better than 1%. Figure S5 shows the equations of state directly from the NIST database and obtained by integrating in Eq. (5) for the approximation $1 + \xi(P) = 1 + \xi_0$. The maximum difference between the curves reaches 1% at the maximum pressure of 0.8 GPa. This result is comparable to the results of extrapolation for propylene glycol. Here, it is appropriate to note that the pressure dependence of methanol density for methanol is close to that for propanol (see Fig. S5 and Fig. 2 in the paper).

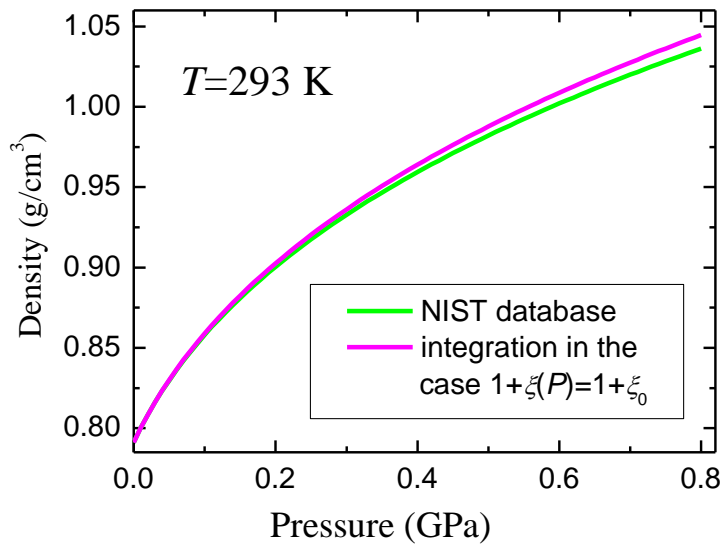


Fig. S5. Pressure dependences of the density ρ of liquid methanol at room temperature 293 K.

S5. Relation between adiabatic and isothermal bulk moduli in glasses at $T = 77$ K

In the case of glasses, the difference between B_S and B_T moduli is much smaller. We did not find the full set of parameters for Eq. (2). However, considering the temperature dependences of these parameters for all three substances similar, it is easy to estimate a change of ξ during transition from the room-temperature liquid to the low-temperature glass. The thermal expansion coefficient undergoes the greatest change during the liquid-glass transition, decreasing by factor

≈ 4.5 in the case of glycerol,³¹ and this is the most significant contribution to the decrease of ξ . Increase of the adiabatic bulk moduli B_s by 2-3 times (Fig. 3 in the manuscript) and decrease by ≈ 3 times of the heat capacity c_p in the case of n-propanol^{24, 26} as example is partially compensated by temperature decrease by more than 3 times. Increase of the density with pressure does not play a significant role, but still decreases the value of ξ . Taking into account all these factors, we obtain that the value of ξ in the low-temperature glass is by an order of magnitude less than that in the liquid phase. Note that for the majority of atomic solids the value of ξ lies within 1-2% even at room temperature.³²

S6. Pressure dependences of ultrasonic velocities at 77 K

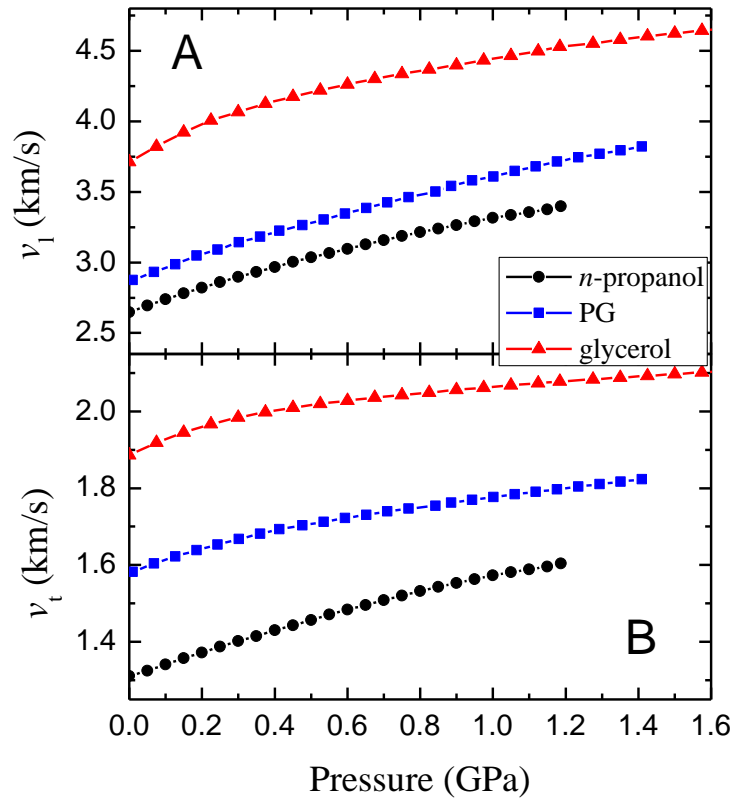


Fig. S6 Pressure dependences of the longitudinal (A) and transverse (B) wave velocities for n-propanol, propylene glycol, and glycerol at the liquid nitrogen temperature.

S7. Dielectric loss and ultrasound attenuation at 10 MHz: Difference in the dynamics of monohydroxy, dihydroxy, and trihydroxy propane alcohols.

The structural difference of the hydrogen bond networks (HBN) in the propane-base alcohols is illustrated by comparison of the dielectric loss and ultrasound attenuation in the supercooled liquids. Unfortunately, we can't detect exactly the temperature of the ultrasound attenuation maximum T_{US} (at 10 MHz in our case) because of technical features of the high-pressure piezometer, when the useful signal is suppressed by parasitic interferences. Nevertheless, our approximation T_{US} (in terms of transmission in Fig. S7) is quite acceptable comparing with literature data available for glycerol.³³ In Fig. S7, we also show temperatures of the dielectric loss maximum at 10 MHz T_{DL} for n-propanol,³⁴ PG,³⁵ and glycerol,³⁶ taking into account temperature shifts for pressure 0.1 GPa (~ 5 K) following the glass transition temperature vs P dependences $T_g(P)$.^{26, 28, 29, 37} T_{US} and T_{DL} coincide quite well in the case of non-hydrogen bonded glass former, using propylene carbonate as example.³⁸ In n-propanol, situation changes radically, and the difference between T_{US} and T_{DL} reaches ≈ 60 K (Fig. S7). The complicated relaxation dynamics is typical for the monohydroxy alcohols^{34, 39-43} and experimentally. Despite strong hydrogen bonding, the difference between T_{US} and T_{DL} in glycerol is much smaller and equals about 5 K that corresponds to ratio of relaxation times ≈ 2 .³⁶ This means that HBN of glycerol is much more isotropic in contrast to the chain-like HBN of n-propanol and directly confirms the three-dimensional nature of HBN in glycerol.

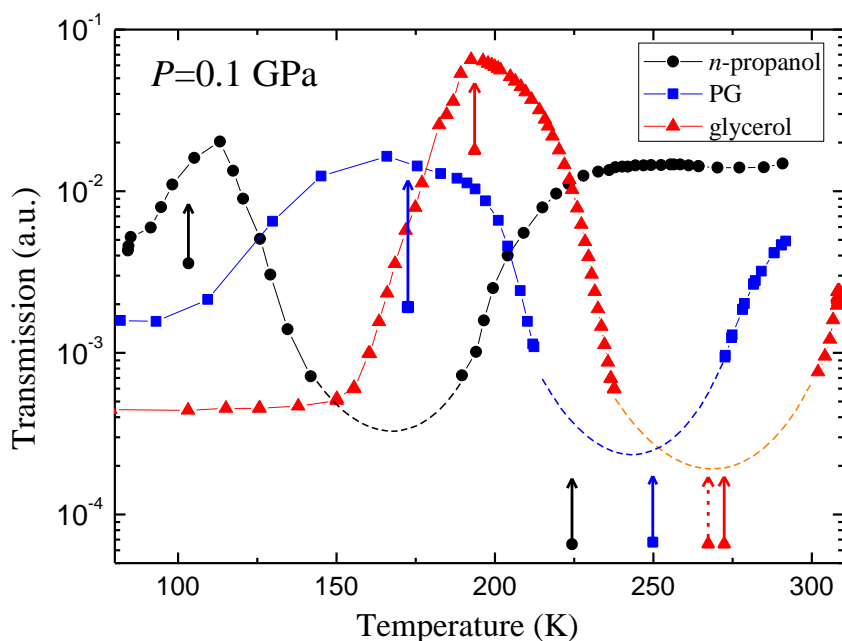


Fig. S7. Temperature dependences of the longitude wave transmission through the experimental assembly with the n-propanol, PG, and glycerol samples near atmospheric pressure (0.1 GPa). Dashed lines correspond to the approximation of the transmission minima. The three upper arrows position the glass transition temperatures. The lower arrows correspond to the maximums of dielectric loss at 10 MHz (see the text) except the dashed arrow corresponding to the maximum of ultrasound attenuation in glycerol at 10 MHz.³³ Symbols at the beginning of arrows correspond to the substances in the legend.

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