Ultrasonic study and molecular dynamics simulation of propylene glycol at pressures up to 1.4 GPa

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Abstract
We report ultrasonic measurements of the density and bulk modulus of propylene glycol at room temperature and at the temperature of liquid nitrogen up to a pressure of 1.4 GPa. We perform molecular dynamics simulations with two different force fields—COMPASS and Charmm. We show that the COMPASS force field reproduces the experimental data with high accuracy. For this reason we employ this force field to analyze the microstructure and hydrogen bonding in the system. We find that the number of hydrogen bonds does not depend on pressure.

1. Introduction
Propylene glycol (PG) is an important liquid for many technological applications, including food industry, resin production, pharmacy, etc. It is also widely used as an antifreeze. For this reason, the properties of PG are of great importance and were studied in numerous works. Nevertheless, a lot of the properties of PG are still poorly understood.

Propylene glycol has a chemical formula of C₃H₈O₂. It is a molecular liquid, which can be easily transformed into glass (the glass transition temperature at ambient pressure is $T_g = 165$ K). A molecule of PG contains two hydroxyl groups, which makes it possible to form hydrogen bonds (H-bonds) in PG. Although H-bonds are weaker than other types of bonds they can strongly affect the properties of a liquid [1–4]. H-bonds can affect orientational correlations between molecules of the liquids and glasses. The relaxation dynamics of H-bonds strongly affects the dynamic properties of liquids. H-bonds can also be responsible for the properties of the liquid as a solvent, as assumed in the case of water [5]. Apparently, a lot of attention of researchers was paid to the investigation of H-bonding in different liquids, both experimentally and theoretically. For instance, H-bonds in liquid alcohols were experimentally studied in [6–14]. These works were complemented by molecular dynamics simulation [15–17]. However, the problem of the behavior of H-bonds still remains unclear, since different works give different, sometimes opposite results (see, for instance, [18–22] for hydrogen bonds in methanol).

In the present work we perform ultrasonic measurements and molecular dynamics simulations of PG at room temperature and at the temperature of liquid nitrogen up to a pressure of 1.4 GPa. We measure the equation of state, compressibility and its pressure derivative and compare the results with the computer simulation. Molecular dynamics simulation also allows us to monitor the microscopic structure of PG and evaluate the number of H-bonds in a wide range of pressures.

2. System and methods

2.1. Experimental methods
The experimental part of the work was carried out using a high-pressure ultrasonic piezometer. It was created on the basis of a press and a piston - cylinder high-pressure chamber, placed in a thermostat for low-temperature measurements [23, 24]. This setup makes it possible to carry out experiments up to a pressure of 2 GPa and in the
temperature range of 77–310 K both in the isothermal compression and isobaric heating regimes. In this work, we performed isothermal compression up to 1 GPa at a constant temperatures of 77 K (liquid nitrogen temperature) and 295 K (room temperature). The pressure measurement error was no more than 0.05 GPa, i.e. 5%, and the temperature was controlled with an accuracy of 1 K. To measure the temperature, we used four copper - constantan thermocouples: two of them were glued in the immediate vicinity of the sample and the other two were glued to punches that pressed on the sample, to control the temperature gradient. Since propylene glycol is a liquid under normal conditions, we used capsules to store the substance. A capsule is a thin-walled Teflon cylinder with an outer diameter of 18 mm and an inner diameter of 16 mm, which is closed on both sides with copper caps 1 mm thick and a rubber ring as a seal. Propylene glycol 99.5% pure was purchased from Sigma-Aldrich. The capsule with the substance was placed in the high-pressure chamber and compressed from both sides by punches, on the ends of which lithium niobate piezoelectric plates were glued. They were both generators and receivers of an ultrasonic signal. Different plates with different thicknesses and resonant frequencies of 5 and 10 MHz were used for longitudinal and transverse ultrasonic waves, respectively. The transit time of ultrasound through the sample was measured with an accuracy of 1 ns. The length of the sample was also measured using two micrometers with an accuracy of 5 μm. The ultrasonic velocity was calculated from the length and transit time; then, in the approximation of a homogeneous isotropic medium [25, 26] the adiabatic bulk modulus $B_s$ was calculated:

$$B_s = \rho v_l^2 - \frac{4}{3} \rho v_t^2,$$

where $\rho$ is the density the substance and $v_l$ and $v_t$ are the longitudinal and transverse ultrasonic velocities, respectively.

In Supplementary materials we describe some details of the experimental determination of the density of PG.

2.2. Molecular simulation
In the computational part of the work, we simulated a system of 1000 molecules of PG in a cubic box with periodic boundary conditions. Two different force fields (FFs): COMPASS [27] and Charmm [28] were used. Figure 1 shows a molecule of PG with the notation of all atoms.

In both FFs the system was equilibrated for 1 ns with the time step $dt = 0.1$ fs. Then the system was simulated for 2 ns to determine its properties. The bonds involving hydrogens were constrained via the Shake algorithm [29]. First, the system was simulated at a temperature of $T = 295$ K at several densities in the canonical ensemble (constant number of particles $N$, volume $V$ and temperature $T$). The densities were selected to cover the whole interval of the experimental densities and to take slightly lower and slightly higher ones. The equation of state was calculated and compared to the experimental data. Since the experimental results are obtained in the form of

\[ \text{Figure 1. An image of a molecule of PG with the notation of atoms.} \]
the pressure dependence of the density, we convert the simulation results into the $\rho(P)$ form although the density is fixed and the pressure is calculated. This equation of state was approximated by polynomial functions to calculate the isothermal bulk modulus $B_T = \rho \left( \frac{dP}{dT} \right)_T$ and the isothermal pressure derivative $\left( \frac{d\rho}{dT} \right)_T$. The details of the approximation are given in Supplementary materials.

When the simulation at $T = 295$ K was finished, the system was quenched to a temperature of 77 K in 5 ns, i.e. at a cooling rate of $4.36 \cdot 10^9$ K/s. Equation of state (EoS), bulk modulus and pressure derivative were calculated at the low temperature too.

The structure of the system was characterized by center-of-mass radial distribution functions (RDFs) and partial radial distribution functions of different species (see figure 1).

Hydrogen bonding (H-bonding) in PG is discussed. Two definitions of H-bonds were discussed in the book [30]: an empirical definition and a definition based on the theory of chemical bonding. In the case of empirical definition the H-bond between the hydrogen atom in an A-H group and an electronegative atom in the same or another molecule occurs if two conditions are fulfilled: (a) there is an evidence of formation of a bond (chelation of association) and (b) there is an evidence that this bond involves a proton which is already bonded to the atom A. The definition based on the theory of chemical bonding can be formulated as the following: a hydrogen bond occurs between an A-H group (proton donor), where A is an electronegative atom and a proton acceptor group B, which is a lone pair of an electronegative atom or a π bond of a multiple bond (unsaturated) system [30].

In the molecular dynamics simulation, the presence of H-bonds is typically analyzed in terms of either a geometric criterion, i.e. if the distance between O and H atoms and the angle in the O - H - O triangle are below some cutoff values or an energy criterion, i.e. the interaction energy between H and O atoms is above a certain minimum value. Such method of H-bond identification is based on the empirical definition discussed above. Several equivalent geometric definitions of H-bonds based on different distances and angles in the O - H - O triangle are possible (see [31] for a detailed discussion). In the present paper we adopted the $r - \alpha$ definition from [31]; i.e. we assume that an H-bond is formed if the distance $r$ and the angle $\alpha$ are below the respective cutoff values (see figure 2). The distance cutoff is taken as the first minimum of the O - H radial distribution function $r_{\text{cut}} = 3.7\AA$ and and the cutoff angle is $\alpha_{\text{cut}} = 30^\circ$. Only the hydrogens from hydroxyl groups are taken into account, since other hydrogens are not polar enough to form H-bonds [32].

All simulations were performed using the LAMMPS simulation package [33].

3. Results and discussion

Figure 3 shows experimental data in comparison with the molecular dynamics simulations with the COMPASS and Charmm force fields. One can see that the simulation with the COMPASS force field perfectly reproduces the experimental data at room temperature up to a pressure of 0.5 GPa and lies within the experimental error bars up to about 0.8 GPa. At the same time time, the experimental density at pressures above approximately 0.5 GPa is higher than the simulated one. This discrepancy can be due to several reasons. In particular, the ultrasonic measurements of PG were carried out under both compression and decompression. The intrinsic friction of the setup leads to an overestimation and underestimation of the pressure under compression and decompression, respectively. As a result, we observe a hysteresis loop, which is eliminated by averaging of the results. However, this method works accurately only in the pressure interval of 0.2–0.7 GPa. Errors can be due to the uniaxial compression in the low pressure regime and to a very high friction in the high pressure one. Thus, the discrepancy between the theoretical and experimental densities at high pressures can be explained by the
increased experimental error in pressure measurements. For this reason, we may suppose that experimental
densities are slightly overestimated at high pressures, and the values obtained in the COMPASS FF simulation
are closer to the real ones. Unfortunately, we are not aware of any measurements of the EoS of PG at high
pressures by another experimental method and therefore we cannot verify our assumption by the direct
comparison of the data.

The molecular dynamics simulations with the Charmm FF strongly underestimate the density at
$T = 295\,\text{K}$ by about 10%, which we consider as an unsatisfactory result.

The situation at $T = 77\,\text{K}$ is reversed. In this case, the COMPASS FF gives very unsatisfactory results, while
the EoS obtained with the Charmmm FF is close to the experimental one. The failure of the COMPASS FF at the
low temperature is not surprising because this FF was parametrized on the data at room temperature [27]. Good
agreement of Charmm FF data with the experimental ones is most likely accidental.

At the same time the derivative of the COMPASS FF EoS at $T = 295\,\text{K}$ is larger than that for the experimental
EoS, while the slope of the Charmmm FF EoS is close to the experimental one. Figure 4(a) shows the bulk modulus
$B_T$ obtained with these two force fields in comparison with the experimental data for the modulus $B_S$. Although
we calculate the isothermal modulus in the molecular dynamics simulation and the adiabatic modulus from
experimental data, as shown in the Supplementary materials of [24], these moduli are almost indistinguishable
at $T = 77\,\text{K}$ and deviate from each other within 10% at room temperature. For this reason such a comparison is
possible. One can see almost perfect agreement of the Charmm FF data with the experimental ones for the
pressures above 0.2 GPa, while the COMPASS FF overestimates $B_T$ comparing to the experimental results.
Experimental data for the bulk modulus suggest that the pressure derivative \( \left( \frac{dB}{dP} \right)_T \) in the studied pressure range is almost constant close to 8.0. This value of the pressure derivative corresponds to a Lennard-Jones (LJ) system. Consequently, one can assume that the interaction between PG molecules can be roughly approximated by the LJ potential.

The pressure derivatives from the molecular dynamics simulation demonstrate a more complex behavior (see figure 4(b)). Although the pressure derivative from the COMPASS FF simulation at \( T = 295 \) K is not constant, but it asymptotically approaches a value of 8.0. For this reason, one can expect that the interaction potential of PG molecules approaches the Lennard-Jones potential with increasing pressure.

In order to verify the above assumption, we calculated the RDFs of centers of mass of PG molecules along the \( T = 295 \) K isotherm with the COMPASS FF. These RDFs are shown in figure 5. According to this figure, the RDF of centers of mass of PG molecules cannot be described by the Lennard-Jones model for two reasons: (i) a pre-peak exists next to the first peak of \( g(r) \) and (ii) the first peak of \( g(r) \) has a shoulder on its right side. At the same time one can see that both effects are weakened as the pressure increases. Basing on this one can expect that the center-of-mass RDF of PG with a further increase in the pressure can approach the RDF in the Lennard-Jones system.

Finally we are going to discuss hydrogen bonding in PG. The formation of a hydrogen bond requires a polar hydrogen atom. In the PG molecule it corresponds to the H12 and H13 atoms, which are bonded to oxygen atoms in hydroxyl groups (see figure 1). The hydrogen atoms belonging to CH3 groups do not form hydrogen bonds because of their small polarity \([32]\). Figure 6 shows the oxygen - hydrogen RDFs at two pressures. One can see that the first minimum of the RDF in all cases corresponds to \( r_{\text{min}} = 3.7 \) Å. For this reason we choose this distance as a cutoff distance for the hydrogen bond formation. Figure 7 shows the RDFs of oxygen pairs at two pressures.
Figure 5. Radial distribution functions of centers of mass of PG molecules at $T = 295$ K obtained with the COMPASS FF. The inset enlarges the first peak of $g(r)$.

Figure 6. Radial distribution functions of hydrogen - oxygen pairs at $T = 300$ K and (a) $P = 0.573$ GPa and (b) $P = 1.28$ GPa. The notation of the atoms is shown in figure 1.
pressures. One can see that the oxygen atoms prefer to orient with the same atoms (either O₆–O₆ or O₉–O₉ pairs). The influence of the pressure on these RDFs is weak.

Our calculations show that at T = 295 K the number of hydrogen bonds does not depend on the pressure: at all studied pressures the number of hydrogen bonds is within 600–640 in the system of 1000 molecules, i.e. a bit more than 0.5 bonds per molecule. Such a small number of hydrogen bonds does not allow the formation of a network.

A common problem of the definition of H-bonds in terms of geometric criteria is their strong dependence on the choice of cutoff parameters. The conventional approach to the choice of r_cut is based on the first minimum of the O - H partial RDF. However, there is no such a simple criterion for the cutoff angle. The cutoff angle in our simulations strongly influences the results. For instance, if we take α_cut = 40° the number of H-bonds is doubled and becomes about 800–860 bonds per 1000 molecules of PG. However, the number of H-bonds obtained with any chosen cutoff parameters very weakly depends on the pressure.

4. Conclusions

In the present study we have performed an ultrasonic measurements and molecular dynamics simulations of the equation of state of propylene glycole. We have shown that the COMPASS force field successfully reproduces the experimental densities. For this reason we have chosen this force field to analyze the microscopic properties of propylene glycole. Using the geometric criterion, we have calculated the number of hydrogen bonds in the system and find that it does not depend on the pressure. The number of hydrogen bonds per molecule is about 0.6.
Further we are going to study the oligomers of propylene glycol to monitor the influence of the size of the molecule on the equation of state, bulk modulus and hydrogen bonding in the system.

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Data availability statement

The data cannot be made publicly available upon publication due to legal restrictions preventing unrestricted public distribution. The data that support the findings of this study are available upon reasonable request from the authors.

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