

Pressure effects in the properties of simple monohydric alcohols. Lessons from molecular dynamics simulations of united atom type UAM-EW model

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We explore the pressure dependence of a set of properties of simple monohydric alcohols, namely of methanol, ethanol and 1-propanol, by using isobaric-isothermal molecular dynamics computer simulations. A recently proposed united atom, non-polarizable force field for each of alcohols [V. García-Melgarejo et al., J. Mol. Liq., **323**, 114576 (2021)] is applied. Accuracy of the force field is evaluated by comparing the simulation results and available experimental data from the literature. Specifically, the density of alcohols upon increasing pressure, the isothermal compressibility, the static dielectric constant and self-diffusion coefficient are investigated starting from 1 bar up to 3 kbar. Evolution of the microscopic structure under pressure is discussed in terms of the pair distribution functions and some coordination numbers. Conclusions of the present modelling and necessary developments to consider in future work are commented on.

Key words: *molecular dynamics, methanol, ethanol, 1-propanol, pressure, density, dielectric constant*

1. Introduction

This manuscript is dedicated to the memory of our close friend and long-term co-worker over the past decades Prof. Stefan Sokołowski who passed away in 2024, unfortunately. We are deeply sad because of this loss. Stefan Sokolowski made important contributions to the statistical mechanical theory of fluids and mixtures. Specifically, his scientific interests were focused on the theory of inhomogeneous associating fluids and mixtures with and without electrostatic interactions [1–3]. He was eager to discover novel features in the behavior of these systems and to develop appropriate methodological tools to describe them. Computer simulation approaches, such as the Monte Carlo technique, molecular dynamics and dissipative molecular dynamics, besides entirely theoretical methods, were the focus of his interests as well. His area of research also involved analyses of relations between theories and experimental studies [4] and apparently very distant complex systems [5–7].

Our present report is motivated by several factors. Namely, in [8] we explored the influence of pressure on some properties of neat methanol very recently. Molecular dynamics simulations have been performed by using three models of methanol to validate theoretical predictions for the microscopic structure in comparison with the results of X-ray and neutron diffraction experiments from ambient pressure, 1 bar, up to gigapascal pressures. This research has been stimulated by previous experimental and computer simulation investigations of the behavior of water and water-alcohol mixtures at high pressures with particular emphasis on the evolution of the hydrogen bonding network.

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On the other hand, previous work from this laboratory was focused on compositional trends of the behavior and mixing of species in water-methanol mixtures dependent on temperature and pressure [9]. However, several issues concerning pressure effects remained out of attention of the authors.

Finally, it is worth mentioning that methanol-water liquid mixtures at room temperature and atmospheric pressure are among the most extensively studied hydrogen-bonded liquids. In order to extend previous observations, composition aspects of mixing of water and alcohol species were investigated by considering ethanol (EtOH) and 1-propanol (PrOH) rather than MeOH-water solutions in [10]. That work, however, was restricted to ambient pressure, 1 bar, and room temperature, 298.15 K.

Having all the above mentioned issues in mind, in the present work, we would like to present very fresh results concerning pressure effects on some basic properties of three alcohols, MeOH, EtOH and PrOH. We employ molecular dynamics simulation as methodological tools and perform comparisons of theoretical predictions with available experimental data from the literature. We are convinced that insights into the microscopic structure, thermodynamic, dynamic and dielectric properties of the systems in question from simulations not only complement various experimental data but lead to a more profound understanding of various properties. Moreover, present simulation findings may stimulate experiments for the structure at high pressures that are not available up to our best knowledge, e.g. for neat EtOH and PrOH and their mixtures with water and/or with organic liquids. In addition, the simulation results for a given model can definitely guide the development of a more sophisticated and more accurate force field for alcohol species.

The most important, initial step of computer simulations methodology lies in the design of an appropriate force field. The intramolecular structure of alcohol species in many cases may be and is considered at different levels of sophistication, from simple united atom models to all-atom and to polarizable ones. Ab initio calculations have been attempted for alcohols as well. However, an increasing level of complexity of the models is not necessarily accompanied by the improvement of predictions for the basic properties. Besides, sophisticated models require expensive calculations.

In this work, we use a simple united atom model for each of alcohols under study, namely the UAM-EW type model [11] (note that the potential model denoted as UAM-I in [8] is identical to UAM-EW). Its parametrization at 298.15 K and ambient pressure, 1 bar, described very much in detail in [11] involves the fluid density, ρ , the dielectric constant, ϵ , and the surface tension, γ , as target properties. In addition, the model for each alcohol is adjusted to provide a correct miscibility with TIP4P- ϵ water force field [12]. One of the essential merits of the UAM-EW model, in contrast to other models of this type, is that it reproduces three target properties simultaneously, with reasonable accuracy (deviations from the experimental data are less than a few percent) and correct miscibility with water is ensured. However, a detailed analysis of the performance of the model dependent on temperature and pressure has not been performed so far.

2. Models and simulation details

The united atom type, non-polarizable, UAM-EW model [11] for alcohols assumes sites, O, H, CH₂ and CH₃, and is constructed from the interaction potential between all atoms and/or groups. It is considered as a sum of Lennard-Jones (LJ) and Coulomb terms. All the parameters for inter- and intramolecular interactions are given in the supplementary material to [11]. Lorentz-Berthelot combination rules were used to determine cross parameters for the relevant potential well depths and diameters.

Molecular dynamics computer simulations were performed in the isothermal-isobaric (NPT) ensemble at temperature 298.15 K and at pressures in the interval between 1 bar and 3000 bar. We used the GROMACS software package [13] version 5.1.2. The simulation box in each run was cubic, the total number of molecules in all cases was fixed at 3000. As common, periodic boundary conditions were used. Temperature and pressure control was provided by the V-rescale thermostat and Parrinello-Rahman barostat with $\tau_T = 0.5$ ps and $\tau_P = 2.0$ ps, the timestep was 0.002 ps.

The non-bonded interactions were cut-off at 1.1 nm, whereas the long-range electrostatic interactions were handled by the particle mesh Ewald method implemented in the GROMACS software package (fourth order, Fourier spacing equal to 0.12) with the precision 10^{-5} . The van der Waals correction terms

to the energy and pressure were applied. In order to maintain the geometry of molecules the LINCS algorithm was used.

After preprocessing and equilibration, consecutive simulation runs with the starting configuration being the last configuration from the previous run, were performed to obtain trajectories for the data analysis. The results for the majority of properties were obtained by averaging over a set of runs. However, the dielectric constant was obtained from the entire long trajectory. The self-diffusion coefficients of species were calculated from the best slope of the mean squared displacement as common.

3. Results and discussion

3.1. Density and isothermal compressibility

The dependence of density for each alcohol on pressure from molecular dynamics simulations and comparison with experimental data are shown in three panels of figure 1.

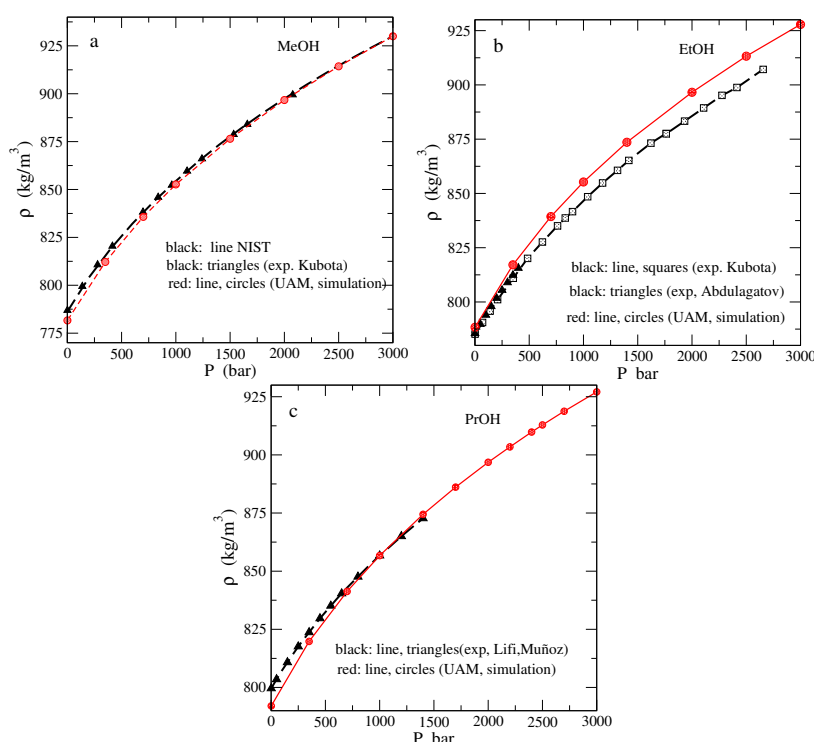


Figure 1. (Colour online) Panels a, b and c: Methanol, ethanol and propanol density on pressure at 298.15 K, respectively. The simulation results are for the UAM-EW united atom models. The experimental data are from [14–16] (panel a), [17, 18] (panel b), and [19, 20] (panel c).

The plots for each alcohol are shown separately for better visualization, because the absolute values are close to each other. The experimental data in panel a are from [14–16] and in panel b from [17, 18]. Finally, the experimental values of PrOH density on pressure are taken from [19, 20]. The best agreement between the simulation results and experimental points is observed for liquid MeOH. On the other hand, the UAM-EW model overestimates the growth of the EtOH density with increasing pressure, in comparison with experiments. By contrast, the density for liquid PrOH is underestimated at low pressures. Better agreement with experiment is observed at intermediate pressures, in the interval between 0.8 kbar and 1.4 kbar. Apparently, at high pressures the model behaves reasonably, experimental data are not available for even higher pressures. Still, an overall performance of the UAM-EW model can be termed as entirely satisfactory for three alcohols over a wide pressure range.

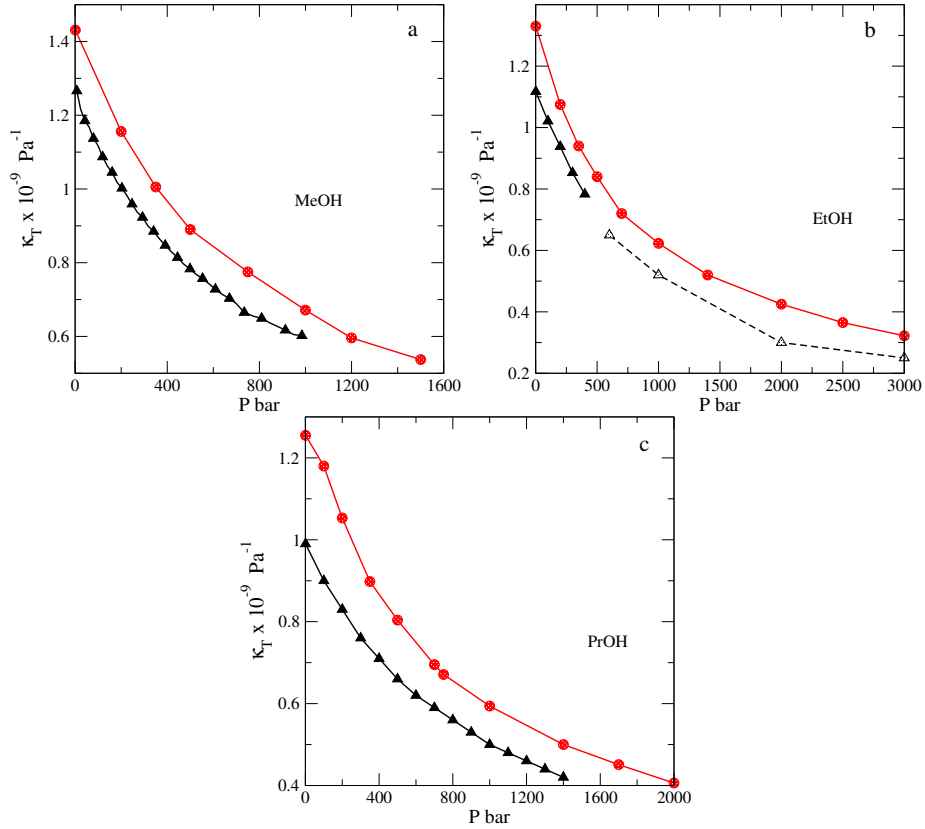


Figure 2. (Colour online) Pressure dependence of the isothermal compressibility for MeOH (panel a), EtOH (panel b), and PrOH (panel c). The experimental data are from [23] for MeOH; from [24] (solid triangles) and [17] (hollow triangles) for EtOH, respectively; and from [20] for PrOH.

It is worth noting that in the case of MeOH, the TraPPE model [21] and the MeOH OPLS/2016 model from [22], provide quite accurate descriptions of density on pressure as documented in our recent contribution [8]. On the other hand, we are not aware of computer simulation results for density on pressure using the TraPPE model for EtOH and PrOH.

In order to get additional insights into the performance of the UAM-EW models for density in the temperature-pressure plane, we illustrate the isothermal compressibility on pressure for MeOH, EtOH and PrOH in figure 2. From the previous figure 1, that describes the $\rho(P)$ behavior, we learned that the discrepancy between simulation data and experimental results is quite small for all thermodynamic states studied. However, in all cases shown in figure 2, the differences between theory and experiment for isothermal compressibilities are more pronounced in terms of absolute values. Still, the shape of the curves for $\kappa_T(P)$ is very similar from simulations and experiment, indicating an entirely satisfactory performance of the models for this specific property. It is worth mentioning that isothermal $\rho(P)$ measurements fitted to various equations of state are frequently used to elaborate the compressibility values in experimental works.

We do not discuss trends of behavior of the isoentropic compressibility, κ_S , and the coefficient of isobaric thermal expansion, α_P , in the present work. Their behavior will be considered in a separate study to explore temperature and pressure trends of a more complete set of properties related to fluctuations. Now, we proceed to the results for the dielectric constant on pressure.

3.2. Dielectric constant

The dielectric constant is one of the most important physico-chemical properties of a given liquid, as it determines to a great extent the mixing properties with other substances. Our results for ε follow from the time-average of the fluctuations of the total dipole moment of the system [25], as common in simulations,

$$\varepsilon = 1 + \frac{4\pi}{3k_BTV} \left(\langle \mathbf{M}^2 \rangle - \langle \mathbf{M} \rangle^2 \right), \quad (3.1)$$

where k_B is the Boltzmann constant and V is the simulation cell volume.

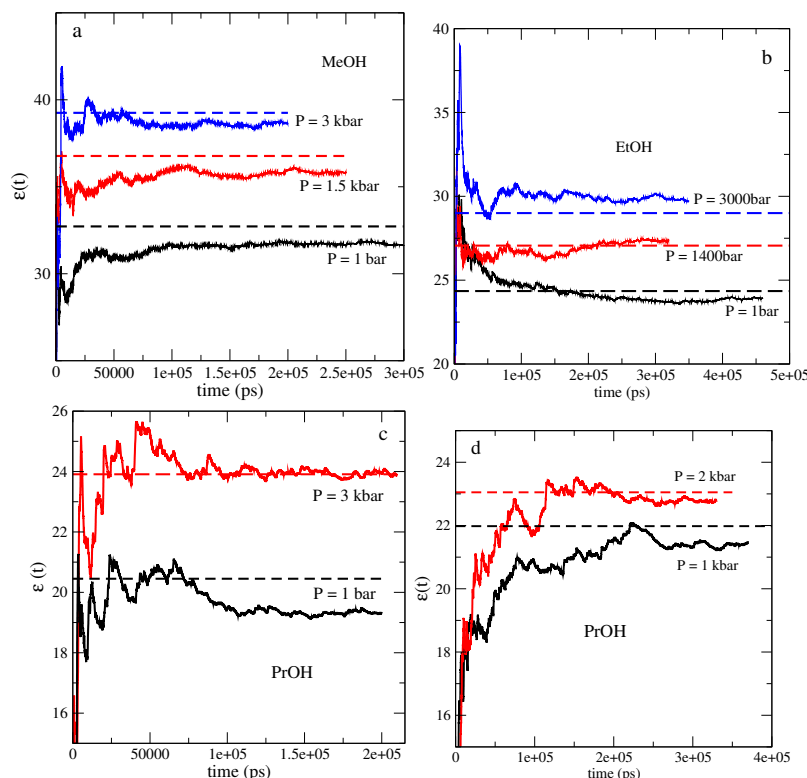


Figure 3. (Colour online) Panels a, b, c and d: Illustration of the calculations of dielectric constant of methanol, ethanol and 1-propanol at different pressures (indicated in the figure) at 298.15 K. The simulation results are for UAM-EW united atom model. The experimental data (dashed lines in all panels) are from [26].

Technically, the value for ε is deduced from a plateau region of the curves for $\varepsilon(t)$. A few examples illustrating the accuracy of our calculations for the three alcohols under study are shown in figure 3. The experimental data are taken from [26]. Earlier results of measurements of ε for three alcohols are given in [27]. They are in good agreement with [26] for MeOH and EtOH. For PrOH, the qualitative behavior is similar, just the data from [27] are very slightly lower than those from [26]. Therefore, we restricted our comparisons to the more recent data set. As expected, long runs (trajectories) are necessary to capture the value for the dielectric constant with reasonable accuracy. In the case of MeOH and EtOH (panels a and b of figure 3), the curves for $\varepsilon(t)$ exhibit plateaus after 200 ns approximately. It can be seen that the UAM-EW model slightly underestimates the values for the dielectric constant of MeOH in the entire interval of pressures under study (panel a of figure 3). On the other hand, for EtOH the model either underestimates ε at low pressures, close to ambient pressure, or overestimates it at high pressure values (panel b, figure 3).

The accuracy of calculations for PrOH are illustrated in figures 3c and 3d. In some cases, the $\varepsilon(t)$ curves exhibit more pronounced oscillations (note that the y -axis range is narrower here than it is in panels a and b) comparing to MeOH and EtOH. Perhaps both the re-organization of the non-polar part and the assumed rigidity of the molecules contribute to the rate of decay of polarization fluctuations. Deeper understanding of these issues require extensive studies of dielectric relaxation phenomena — a wide and active area of research in spite of a quite long history for various alcohols [28–33].

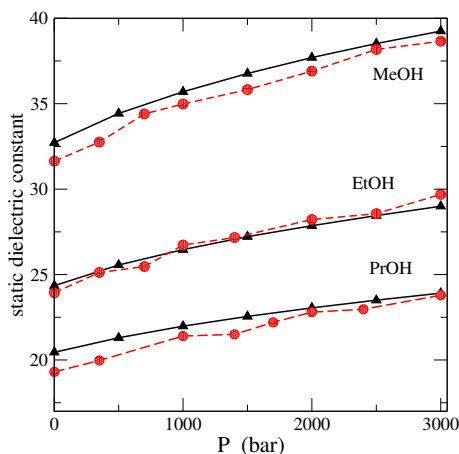


Figure 4. (Colour online) Static dielectric constant of alcohols on pressure at 298.15 K. The simulation results are for the UAM-EW united atom model. The experimental data (solid lines with triangles) are from [26].

A summarizing insight into the dependence of the dielectric constant on pressure for the three alcohols under study is provided by figure 4. In general terms, the UAM-EW model satisfactorily describes the trends of behavior of the static dielectric constant on pressure starting from 1 bar up to 3 kbar. Discrepancy between predictions coming from simulations and experimental data is of the order of a few percent. The dielectric constant increases with increasing pressure for all three alcohols.

However, the increment is most pronounced for MeOH, in comparison with EtOH and PrOH. For this latter system, the growth of ε is the weakest. In fact, trends for density, cf. figure 1, and the dielectric constant with pressure are qualitatively similar. Apparently, the correlations between dipolar moments of molecules become stronger when the average distance between them decreases. We will return to this point below, after discussing the changes of the microscopic structure with increasing pressure.

3.3. Self-diffusion coefficients

Evaluation of the quality of the model frequently involves the results for the self-diffusion coefficient, D . Note, that D has not been considered as a target property within the multistep parametrization of the UAM-EW model [11]. One of the common routes to obtain D , is from the mean square displacement of particles. On the other hand, it may be also calculated from the velocity auto-correlation function. We calculate D by the former procedure, via the Einstein relation,

$$D = \frac{1}{6} \lim_{t \rightarrow \infty} \frac{d}{dt} |\mathbf{r}(\tau + t) - \mathbf{r}(\tau)|^2, \quad (3.2)$$

where τ denotes the time origin. Default settings of GROMACS were used for the separation of the time origins.

The dependence of D on pressure following from simulations, for the three alcohols in question, is shown in figure 5. Besides, this figure contains available experimental data for the sake of comparison. It can be seen that D decreases with increasing pressure for each alcohols in agreement with experimental data. This kind of behavior is expected due to augmenting density with pressure.

For MeOH, the decrement of the self-diffusion coefficient with pressure is larger than for the two other alcohols, EtOH and PrOH, as seen from experimental data and simulations. The values for D for MeOH are underestimated over the entire pressure range compared to experimental results. On the other hand, the agreement between simulations and experiments is much better for EtOH and PrOH.

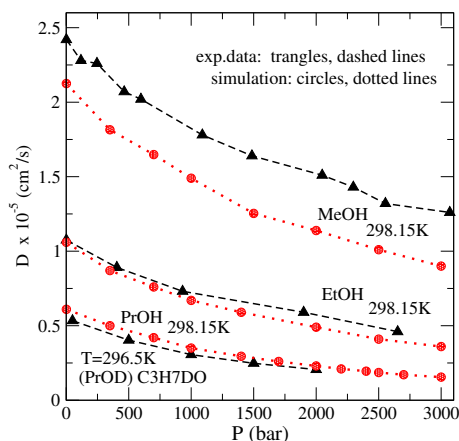


Figure 5. (Colour online) Self-diffusion coefficient of alcohols on pressure at 298.15 K. The simulation results (circles and dotted lines) are for the UAM-EW united atom model at 298.15 K. The experimental data (dashed lines with triangles) are from Hurle et al. [34] (methanol and ethanol at 298.15 K). The experimental data for PrOH are for a C3H7DO sample at 296.5 K from Shaker-Goafar et al. [35].

Undoubtedly, it is worth complementing this type of results for alcohols under pressure by the calculations of viscosity and other dynamic properties as it was discussed in [36]. We hope to extend the present study in this aspect in a future work.

3.4. Microscopic structure

This subsection contains the site-site pair distribution functions (PDFs) for different alcohols and some coordination numbers necessary to interpret microscopic structure.

Concerning the first maxima of the functions shown in figure 6 for MeOH, we would like to mention the following features. The height of the first maximum of $g_{O-O}(r)$ and $g_{O-H}(r)$, panels a and b, respectively, slightly decreases in value, if the pressure increases from 1 bar to 3 kbar. By contrast, the first maximum of $g_{C3-C3}(r)$ and $g_{C3-O}(r)$ (figure 7), increases upon increasing pressure. The first and second coordination shells are well pronounced in the $g_{O-O}(r)$ PDF at 1 bar and at 3 kbar, figure 6a. The third shell is weakly pronounced in both cases.

The maxima characterizing the first shell centered on an oxygen atom in terms of $g_{O-O}(r)$ and $g_{O-H}(r)$, witness that the distances between these atoms do not change. Thus, the first shell remains practically intact upon increasing pressure. However, the characteristic distances describing more distant atoms change. Namely, the second maximum of $g_{O-O}(r)$ shifts to a shorter distance at 3 kbar compared to 1 bar (figure 6a). Changes of the height of the first and the second minima of O-O distribution are small. This behavior confirms a weak distortion of the neighborhood of oxygen atoms and of the arrangement of polar parts of methanol molecules. The $g_{H-H}(r)$ PDF keeps unchanged its principal features with increasing pressure as well, figure 6c. Interpretation of the structure in terms of PDFs for MeOH was elaborated in several previous publications. We would like to attract attention of the reader to the results from [37] and our recent findings [8].

Additional insights into the changes of the O-H coordination with pressure appear from table 1. The first and following coordination numbers are commonly evaluated by integration of the pair distribution

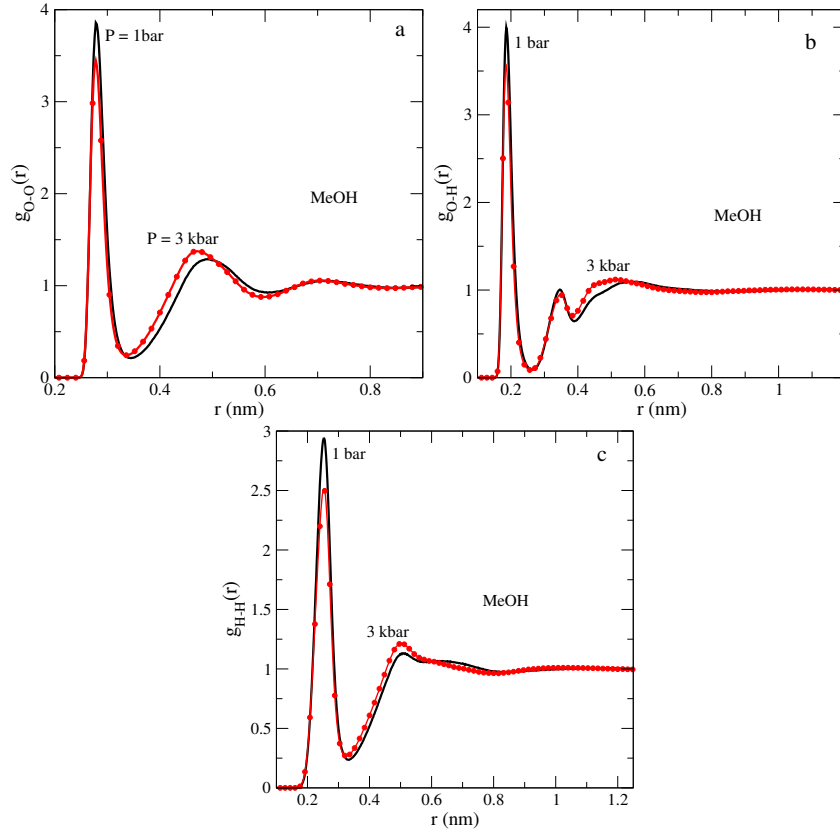


Figure 6. (Colour online) Computer simulation results for the site-site pair distribution functions for liquid MeOH at 1 bar (black lines) and at 3 kbar (red lines) at 298.15 K.

functions up to the first and following minima,

$$n_{ij} = 4\pi\rho_j \int_0^{r_{ij}^{\min}} g_{ij}(R)R^2 dR, \quad (3.3)$$

where ρ_j is the density of species j and $g_{ij}(r)$ is the appropriate PDF. The first coordination number practically does not change with pressure ($n_{\text{OH}}^{(i)} = n^{(i)}$). However, the second coordination number increases, presumably due to increasing density of the system at a higher pressure, 3 kbar. In addition to the data in table 1, we have calculated the average number of hydrogen bonds, n_{HB} , per methanol molecule. It is obtained by using the GROMACS utility with default settings, i.e., the geometric criteria are used. At 1 bar, $n_{\text{HB}} = 1.923$, whereas at 3 kbar, $n_{\text{HB}} = 1.9355$. In conclusion, pressure affects the number of hydrogen bonds between the neighboring molecules quite weakly. This observation is in accordance with our very recent extended discussion in [8] that underlines changes of the cooperative structure of hydrogen bonding network, rather than the influence of pressure on n_{HB} .

Much more pronounced changes of the structure upon increasing pressure are observed in the function $g_{\text{C3-C3}}(r)$, figure 7a. Its oscillations essentially grow in magnitude. At least four coordination shells are seen that witness the trends to form a more ordered structure of non-polar “tails” of methanol molecules. This kind of behavior was observed previously, cf. panels a and b of figure 4 in the [8]. In addition, one can find a very satisfactory agreement of the characteristic distances for this PDF and the following $g_{\text{C3-O}}(r)$ (figure 7b), both with the curves shown in figure 4 from [8] and figure 5 in [37].

Next, we proceed to the EtOH system and describe changes of its structure with increasing pressure in figure 8. The first two panels, a and b, concern the polar part of EtOH molecule, figures 8a and 8b. Changes

Table 1. Location of the first two minima of O-H distribution, and the corresponding coordination numbers, $n_{\text{OH}}^{(1)}$ and $n_{\text{OH}}^{(2)}$, for MeOH at two pressures.

P	$r_{\min}^{(1)}$ (nm)	$n^{(1)}$	$r_{\min}^{(2)}$ (nm)	$n^{(2)}$
1 bar	0.264	1.985	0.389	3.596
3 kbar	0.259	1.991	0.384	3.797

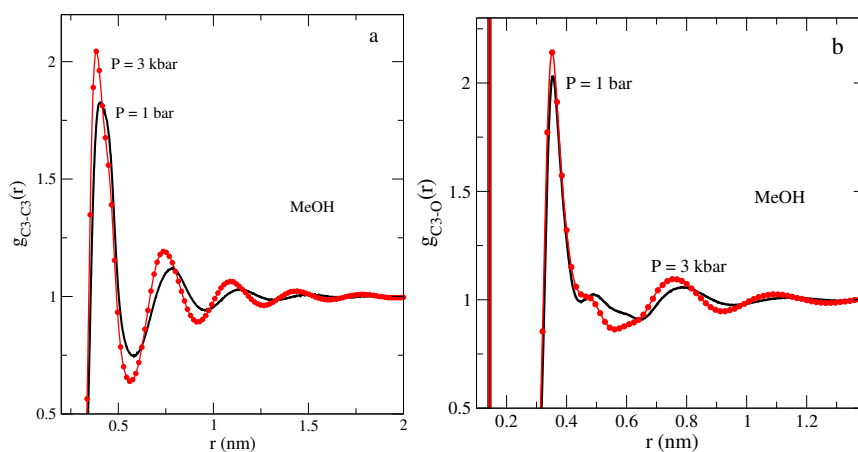


Figure 7. (Colour online) Computer simulation results for the site-site pair distribution functions for liquid MeOH at 1 bar (black lines) and at 3 kbar (red lines) at 298.15K.

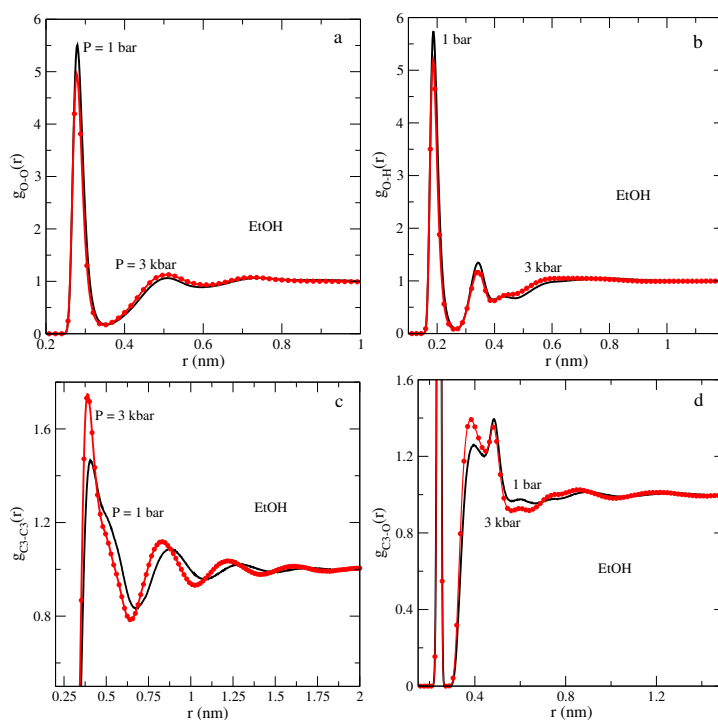


Figure 8. (Colour online) Computer simulation results for the site-site pair distribution functions for liquid EtOH at 1 bar (black lines) and at 3 kbar (red lines) at 298.15 K.

of the first coordination shell in this system in terms of the functions $g_{O-O}(r)$ and $g_{O-H}(r)$ are marginal, in close similarity to MeOH discussed above. However, the shape of the $g_{O-H}(r)$ PDF differs from what was observed for MeOH. Namely, there is a well pronounced second maximum on O-H distribution as an evidence of a “tighter” arrangement of the second coordination shell, in contrast to fluid MeOH. A more complex shape of $g_{C3-C3}(r)$ and $g_{C3-O}(r)$ PDFs (figures 8c and 8d), in comparison with MeOH, is due to the two-site non-polar part of the EtOH molecule comprising CH_2 and CH_3 sites. Moreover, the magnitude of changes of the shape of $g_{C3-C3}(r)$ and $g_{C3-O}(r)$ PDFs upon increasing pressure, are more pronounced in comparison with MeOH. Unfortunately, we are not able to perform detailed comparisons of trends for the microscopic structure upon increasing pressure. The experimental data at high pressure are not available in the literature so far. Apparently, principal features of the structure predicted by the model in question qualitatively agree with findings discussed in [38]. We expect that present findings will stimulate experimental research at high pressures for neat EtOH and its aqueous solutions, similarly to the MeOH system [39].

The effect of pressure on the microscopic structure of PrOH is described in figures 9 and 10. Again,

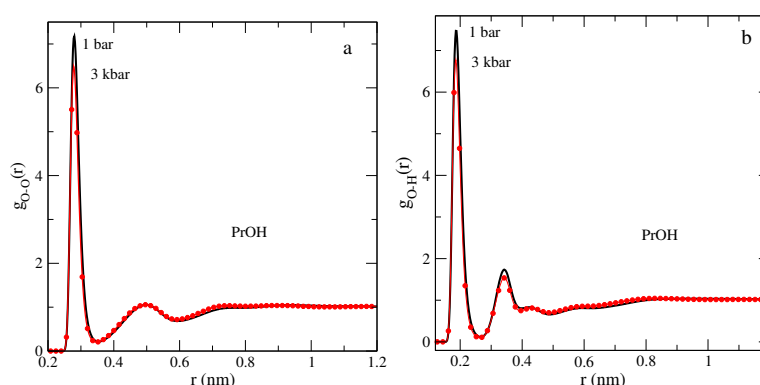


Figure 9. (Colour online) Computer simulation results for the site-site pair distribution functions for liquid PrOH at 1 bar (black lines) and at 3 kbar (red lines) at 298.15 K.

we resort to the evolution of the distribution functions and some coordination numbers. The principal findings can be summarized as follows. The functions describing the distribution of atoms of the polar part of the molecule, O and H (panels a and b, figure 9), respond very weakly to augmenting pressure.

Table 2. Location of the first minima of O-H distribution, and the corresponding coordination numbers for PrOH at two pressures. The distances marked as $2a$ and $2b$ correspond to a minimum on the shoulder of the second shell and to the true minimum between the second and third shell in figure 9b.

P	$r_{\min}^{(1)}$ (nm)	$n^{(1)}$	$r_{\min}^{(2a)}$ (nm)	$n^{(2a)}$	$r_{\min}^{(2b)}$ (nm)	$n^{(2b)}$
1 bar	0.267	1.987	0.397	3.472	0.492	4.853
3 kbar	0.263	1.991	0.395	3.535	0.486	5.115

The average number of hydrogen bonds per propanol molecule, n_{HB} , at 1 bar is 1.937, whereas at 3 kbar it is 1.9512. These numbers at two pressures are close to the first coordination numbers in table II and confirm that the majority of molecules forming the first shell are hydrogen bonded. Moreover, the bonding between the neighboring molecules is marginally affected by the application of pressure on the system.

The structure of the first coordination shell of oxygens remains practically the same at 1 bar and at 3 kbar. Only farther shells slightly change, as manifested in the $g_{O-H}(r)$ distribution (figure 9b), due to the changes of arrangement of the non-polar parts of molecules (figure 10). These non-polar tails of PrOH particles, composed of two CH_2 and one CH_3 sites, noticeably respond to compression of the system figure 10a. In contrast to figure 8d for EtOH, where the intra- and inter-molecular contributions

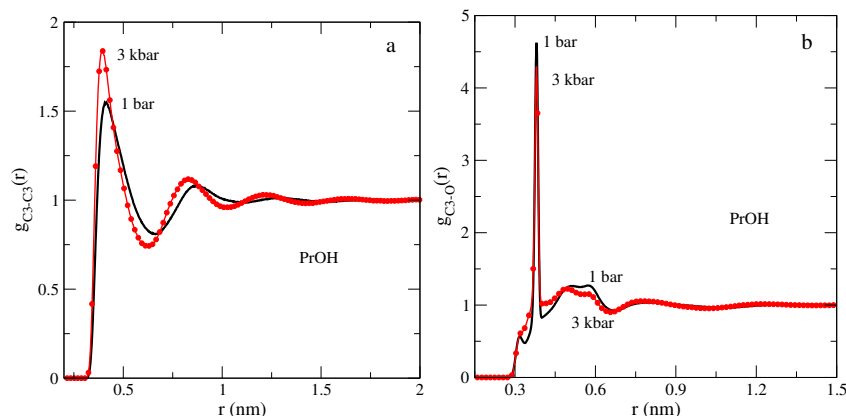


Figure 10. (Colour online) Computer simulation results for the site-site pair distribution functions for liquid PrOH at 1 bar (black lines) and at 3 kbar (red lines) at 298.15 K.

are separated, for PrOH, we cannot separate these terms, i.e., they overlap due to a larger non-polar tail, figure 10b. This issue does not permit to straightforwardly interpret the changes of $g_{C3-O}(r)$ on pressure.

Our final remarks in this section concern the behavior of the distance dependent finite system Kirkwood factor, G_K . The theoretical background of the significance of G_K for dipolar hard spheres was explained in [40] very much in detail. On the other hand, we would like to refer to [41–43] that contain an appealing description of implications for more complex molecules and for fluids with hydrogen bonding. In the present simulations, G_K is calculated similarly to [22],

$$G_K = 1 + \frac{2}{N} \sum_{i < j} \mathbf{u}_i \mathbf{u}_j, \quad (3.4)$$

where N is the number of molecules in the box, $\mathbf{u}_i$ is the unit vector in the direction of the dipole moment of molecule i .

Some issues concerning the models for MeOH were considered in [22, 41, 42] at $P = 1$ bar. Our results for MeOH, EtOH and PrOH, at $P = 1$ bar and $P = 3$ kbar ($T = 298.15$ K) are shown in three panels of figure 11, respectively. In each of the panels, the vertical dashed green lines mark the limits of the first few coordination shells evaluated from the respective minima of the $g_{O-O}(r)$ pair distribution function (from the curves in figures 6a, 8a, 9a and 10a).

The following conclusions may be formulated concerning $G_K(r)$. The first few maxima on $G_K(r)$ correspond precisely to the coordination shells determined by the microscopic structure given in terms of $g_{O-O}(r)$. These indicate preferential parallel alignment of the dipole moments of molecules for each system under study. Nevertheless, the oscillations of $G_K(r)$ are pronounced at larger distances where one cannot identify the maxima and minima of the O-O distribution. This behavior can be attributed to a long-range dipole-dipole interaction and to the cooperative features of the hydrogen bonding in the alcohols studied. The length of non-polar part of a molecule, i.e., the number of sites, influences the shape of $G_K(r)$. For example, it behaves differently at distances $0.5 \text{ nm} < r < 0.9 \text{ nm}$ for MeOH and PrOH, figures 11a and 11c. One can attribute the different behavior of $G_K(r)$ to the shape of $g_{O-O}(r)$, cf. figure 10a. The effect of pressure on the values of $G_K(r)$ is most pronounced for MeOH, in comparison with the other two alcohols, EtOH and PrOH. Nevertheless, one can see that the effect of pressure is negligible at small distances between molecules that correspond to the first coordination shell. Apparently, higher values of $G_K(r)$ at high pressure, 3 kbar, can be attributed to the evolution of cooperative features of hydrogen bonding, because at a “pair level”, the average number of hydrogen bonds per molecule is not affected by increasing pressure from 1 bar to 3 kbar. These issues require additional exploration by using simulations and by experimental research.

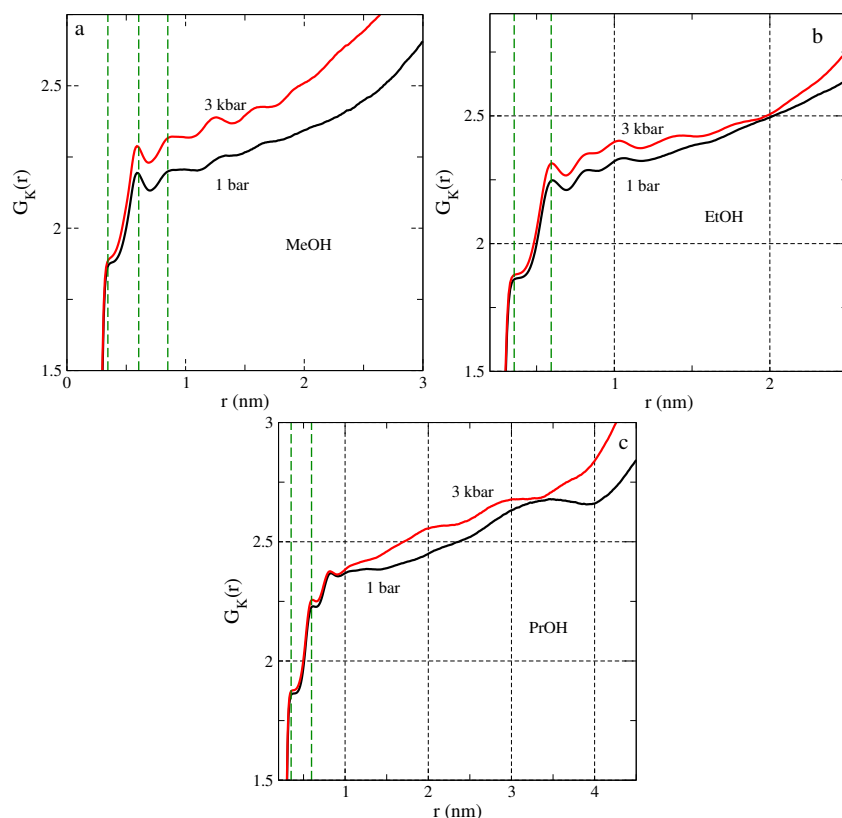


Figure 11. (Colour online) Illustration of the calculations of the distance dependent finite — system Kirkwood factor, $G_K(r)$, r is the distance between the centres of two dipoles. The results for MeOH, EtOH and PrOH are given in panels a, b and c, respectively. The pressures are indicated in the figure, $T = 298.15$ K.

4. Summary and conclusions

To summarize, in the present work we presented computer simulation results concerning the effects of pressure on some properties of three simple monohydric alcohols, MeOH, EtOH and PrOH, by using the united atom type UAM-EW model. The pressure values are in the interval from 1 bar to 3 kbar. A single value of temperature, $T = 298.15$ K was considered. The dependencies of density, isothermal compressibility, dielectric constant and self-diffusion coefficient on pressure were evaluated and compared with experimental data. The model under study yields the results that reasonably well agree with experimental findings. Simulation results are novel and demonstrate validity of the model.

In addition, we illustrated the changes of structural properties of the model for alcohols under pressure, by using site-site pair distribution functions. Their behavior is discussed in terms of coordination numbers. It is shown that the behavior of the finite system Kirkwood factor is related to the coordination shells of the distribution of oxygen sites at ambient and at high pressure.

Undoubtedly, the results of the present study can serve as a guide to complement exploration of the model in various aspects. Namely, one should attempt to describe the adiabatic compressibility and involve experimental measurements of the speed of sound, for the sake of comparison. Heat capacity at constant pressure should be explored as well. Concerning the dynamic properties, future research must involve simulations of viscosity. It is of great interest to complement the description of trends of dielectric constant on pressure from the present work, by the study of dielectric relaxation phenomena. All these issues permit evaluation of computer simulation modelling w.r.t. experimental measurements of thermodynamic and dynamic properties and application of dielectric spectroscopy. Along these lines, one would be able to critically evaluate the validity of the model and attempt construction of a more

accurate force field.

Much work is required to improve the present understanding of the structural properties. Evidently, there are no tools to establish accuracy of the partial (site-site) pair distribution functions. The quality of the entire set of PDFs is commonly evaluated by construction of the total structure factor, $S(Q)$, and comparisons with the results from X-ray and neutron diffraction experimental data at different conditions. This kind of procedure was realized recently for MeOH [8]. Unfortunately, the experimental results for EtOH and PrOH at high pressures are not available at present. One can rely on the relevant data at 1 bar [44, 45] to get preliminary insights. At high pressures one may encounter problems due to the rigidity of the models for EtOH and PrOH. This issue requires additional considerations. Nevertheless, the coordinates files from simulations can be used to perform analyses of the network of hydrogen bonds focusing on the cooperative aspects of bonding in close similarity to [8]. Afterwards, necessary improvements of modelling at the level of united atom and all atom type force fields would become plausible. We do not share the rather pessimistic opinion about the present state of art of modelling of alcohols expressed in [46] (obtained solely from the OPLS and COMPASS force fields for methanol under high pressures) and hope to make progress in solving some of the problems outlined above in future studies.

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Вплив тиску на властивості простих одноводневих спиртів. Уроки молекулярно-динамічного моделювання моделі UAM-EW типу об'єднаного атома

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З використанням ізобарно-ізотермічного комп'ютерного моделювання молекулярної динаміки досліджується залежність від тиску низки властивостей простих одноводневих спиртів, а саме: метанолу, етанолу та 1-пропанолу. Для кожного зі спиртів застосовується нещодавно запропоноване неполяризоване силове поле об'єднаного атома [V. García-Melgarejo et al., J. Mol. Liq., **323**, 114576 (2021)]. Точність силового поля оцінюється шляхом порівняння результатів моделювання та доступних з літератури експериментальних даних. Зокрема, досліджуються густина спиртів при збільшенні тиску, ізотермічна стисливість, статична діелектрична проникність та коефіцієнт самодифузії, починаючи від 1 бар до 3 кбар. Обговорюється еволюція мікроскопічної структури під тиском з точки зору парних функцій розподілу та деяких координаційних чисел. У коментарях наведено висновки цього моделювання та необхідні зміни, які слід враховувати в майбутній роботі.

Ключові слова: молекулярна динаміка, метанол, етанол, 1-пропанол, тиск, густина, діелектрична проникність
