

Hydrogen Bonding in Supercritical Methanol. A Molecular Dynamics Investigation

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The molecular dynamics simulation technique was used to study the hydrogen-bonding structure of supercritical and liquid methanol in a wide range of temperature and pressure. The center of mass and the site–site pair distribution functions (PDFs) were obtained and their temperature and pressure dependence were investigated. Over the temperature and pressure range investigated here we find that the methanol molecules remain highly structured. Specifically, the behavior of the first peaks in O–O, H–H and H–O PDFs reveal the existence of hydrogen bonds in the system. The hydrogen bonds were estimated on the basis of a well-defined geometric criterion. We found that this criterion is in quantitative accordance with the energetic criterion of Jorgensen (Jorgensen, W. L. *J. Phys. Chem.* **1986**, *90*, 1276) concerning the estimation of hydrogen bonds in liquid methanol. The average number of hydrogen bonds per molecule n_{HB} was obtained and compared with corresponding available data from NMR chemical shift measurements. The agreement between experiment and simulation was found to be excellent. The percentage distribution f_i of liquid and supercritical methanol molecules, with $i = 0, 1, 2, 3, \dots$ hydrogen bonds per molecule, has been obtained and analyzed.

1. Introduction

The problem of hydrogen bonding in self-associated liquids and liquid mixtures has been extensively studied for many years.^{1,2} From early studies to recent NMR, neutron-scattering, and other spectroscopic as well as thermodynamic investigations, experimentalists have always striven to gain further insight into the details of hydrogen-bonding structure and dynamics that characterize these molecular systems.³ Of course, this great interest is obviously due to the fact that hydrogen-bonded interactions play an important role in many chemical reactions in solution, phase transition, and generally, in weakly bonded molecules.^{4–8}

Recently, there has been a renewed experimental and theoretical interest in this area of investigation.⁹ The reason for this is that many questions regarding hydrogen bonding in many dense systems still remain unanswered.

Besides the motivation to learn more precisely about hydrogen bonding in liquid and supercritical water (SCW) as well as in aqueous mixtures, investigating pure alcohols and alcohol mixtures is of particular interest, because alcohols may be alternatives to water for a number of reasons.

In a very recent experimental work on this area, Hoffmann and Conradi (HC)¹⁰ studied the hydrogen bonding in supercritical methanol and ethanol up to 450 °C and over a wide range of pressures up to 350 bar. Using a simple model, which utilized the NMR data, they concluded that the chemical shift of the hydroxyl protons reflects changes in the hydrogen bonding of these systems with temperature and/or pressure.

Moreover, although hydrogen bonding is expected to be different in the alcohols compared to water, their results for the three substances have shown a very similar behavior when expressed in terms of reduced thermodynamic variables.

Our study is motivated in part by the previous experimental work of these authors. In the present paper, we report for the

first time results obtained from a molecular dynamics simulation (MD) study of methanol at supercritical (SC) conditions. Our MD treatment is focused upon the macroscopic properties of methanol and specifically upon the short-range intermolecular structure of this fluid at these conditions. We note furthermore that another point of main interest here is to explore the hydrogen-bond network in this molecular fluid as a function of temperature and/or pressure.

To the best of our knowledge, computer simulation studies (CS) for supercritical alcohols have not been carried out up to date. On the other hand, a number of CS studies concerning liquid alcohols and primarily liquid methanol are available in the literature.¹¹ The number of hydrogen bonds per molecule in the case of pure liquid methanol at room and boiling temperature have been reported by Haughney et al.^{11d} and Jorgensen^{11c} using CS techniques. More recently, the density and temperature effects on the hydrogen-bond structure of liquid methanol have been investigated using NMR chemical shifts measurements for the CH₃ and OH groups in conjunction with MD simulations of the system at thermodynamic conditions corresponding to the experiment.^{11j} Results are presented concerning the size and distribution of hydrogen-bonded clusters in the liquid as a function of temperature and pressure. The hydrogen-bond network of ethanol has been investigated by Saiz et al.^{11k} Consequently, the present work may be regarded as an extension of all these previous CS studies with the aim to provide additional information concerning the behavior of this fluid over a wide range of supercritical conditions.

The paper is organized as follows: In section 2 we briefly review the interaction potential model together with some computational details. In subsection 3.1 we report and discuss the simulated pair distributions functions. Subsection 3.2 is devoted to the hydrogen-bonding analysis. Finally, the main results are contained in the concluding section 4.

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TABLE 1: Potential Parameters and Local Charges for the Interaction Sites between Two Methanol Molecules Used in the Present MD Study^a

$\epsilon_{\text{OO}}/K_{\beta}$ (K)	85.5895	q_{O} (e)	-0.700
$\epsilon_{\text{HH}}/K_{\beta}$ (K)	0.0	q_{H} (e)	0.4350
$\epsilon_{\text{MeMe}}/K_{\beta}$ (K)	104.21	q_{Me} (e)	0.2650
σ_{OO} (Å)	3.071	R_{OH} (Å)	0.945
σ_{HH} (Å)	0.0	R_{OMe} (Å)	1.430
σ_{MeMe} (Å)	3.775	<HOMe deg	108.50

^a The cross LJ interaction parameters are obtained using Lorentz–Berthelot combining rules.

2. Simulation Model

The first task in the present work has been to employ an accurate potential model for the interactions between the methanol molecules. For our purpose, we have carried out trial MD runs by using various available models of this fluid at liquid conditions. We found, although most models produce no significant differences in the radial distribution functions, the predicted bulk properties to be unreliable compared with experimental data. Also, our check has shown that the most reliable potential model of liquid methanol is an optimized potential model (OPLS) proposed by Jorgensen.^{11c} On the other hand, it is of particular interest here to see if this OPLS potential is suitable in predicting the properties of the molecular system at supercritical conditions.

This potential is represented by three interaction sites with a short-range Lennard–Jones (12-6) (LJ) part and a long-range Coulombic term. It should be noted here that the methyl group (Me) has been considered as a single interaction site.

$$U(r_{ij}) = \sum \sum \left\{ 4\epsilon_{ij} \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \right\} \quad (1)$$

In eq 1 the sums are over all the pairs of interaction sites ij located at different molecules. q_i and q_j denote the partial local charges and r_{ij} is the distance between two interaction sites. This atomic charge distribution produces an effective dipole moment of 2.216 D which is somewhat enhanced compared to the experimental value in the gas phase (1.7 D).^{11d} The reason for this is to account for the mutual polarization effects. The potential parameters are summarized in Table 1.

The MD calculations were carried out using periodic boundary conditions and the canonical (NVT) statistical mechanical ensemble. The system studied consists of 256 rigid methanol molecules in a cubic box. The bond lengths were $d_{\text{O-H}} = 0.945$ Å and $d_{\text{Me-O}} = 1.430$ Å. The angle Me–O–H was 108.5°.^{11c} The system was simulated at various supercritical thermodynamic points for which experimental P–V–T data are available.¹² Thus, we have carried out nine MD simulations at corresponding thermodynamic states which are listed in Table 2. A full cutoff radius ($r_c = L_{\text{box}}/2$) was applied to all interactions between the species of the system. Also, the long-range electrostatic interactions were treated by using the usual Ewald summation method.¹³ The translation and rotation equations of motions were integrated with leapfrog algorithms.¹⁴ The time integration step was 2.5 fs. Equilibrium was achieved after approximately 75 ps and the simulations were extended subsequently to about 100 ps. The structural and dynamical properties as well as the estimation of the hydrogen bonds have been obtained from the equilibrium configurations.

3. Results

3.1. Intermolecular Structure. The intermolecular structure of the supercritical methanol (SCM) was studied in terms of

TABLE 2: Simulated State Points and Thermodynamic Results Derived from the Simulation of the Supercritical and Liquid Methanol^a

states	experimental			simulation			
	T [K]	ρ [g/cm ³]	P [MPa]	T [K]	P [MPa]	$-U$ [KJ mol ⁻¹]	D [10 ⁻⁹ m ² s ⁻¹]
A	523	0.348	10.0	522.6	11.5	15.71	60.95
B	523	0.516	20.0	522.4	29.2	20.13	34.57
C	523	0.563	30.0	522.4	46.1	21.32	27.90
D	623	0.070	10.0	623.4	9.4	3.24	380.0
E	623	0.260	20.0	623.0	24.8	10.10	98.50
F	623	0.365	30.0	622.1	36.3	13.06	64.80
G	723	0.040	10.0	723.6	6.9	1.50	788.0
H	723	0.200	20.0	723.3	30.1	6.77	150.0
I	723	0.250	30.0	723.3	37.6	8.12	118.0
liquid	298	0.78664	0.10	297.5	-2.5	35.46	3.10

^a The estimated errors were maximal: ± 3 K for T , $\pm 1\%$ for U , and $\pm 12\%$ for P .

pair distribution functions (PDFs). Moreover, with the aim of comparing the structural directing effects of the different thermodynamic states, these functions were also obtained for the liquid methanol at room temperature and normal pressure. All these functions have been constructed for distances up to about 10 Å with a resolution of 0.1 Å for all states of interest.

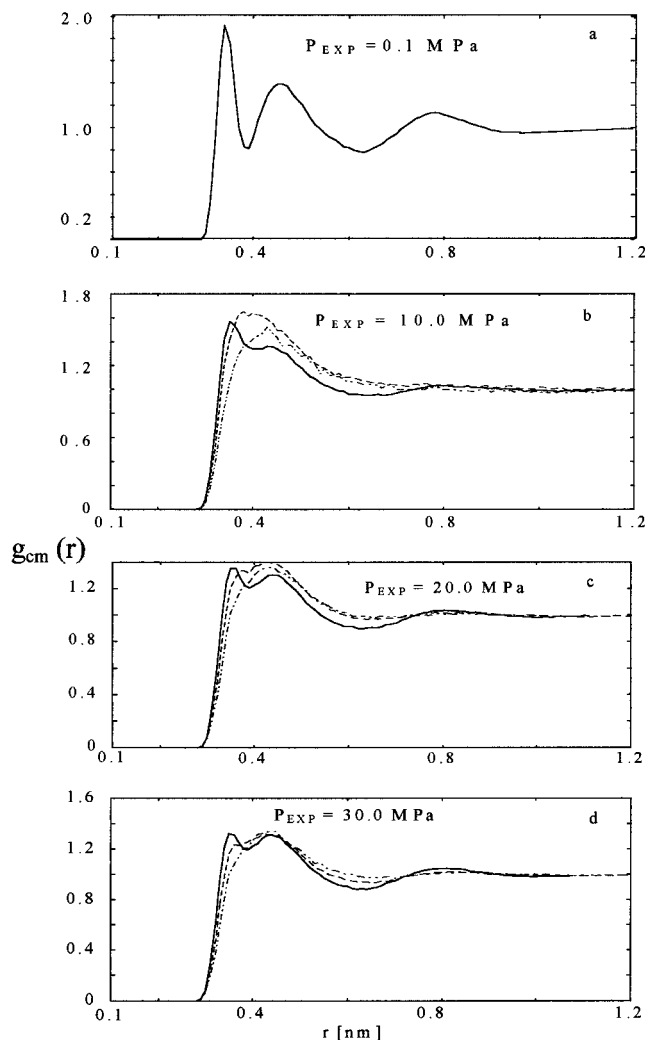
The center of mass (COM) PDFs are displayed in Figure 1b,c,d together with the corresponding function of liquid methanol depicted in Figure 1a. The characteristic extrema (positions and heights of the first peak) of these PDFs are collected in Table 3.

Figure 1 shows how the height and the shape of the main peak in $g(r)$ for the COM–COM methanol pairs varies with temperature at constant pressure and vice versa. Also shown in Figure 1 is the variation of these functions on going from liquid to supercritical conditions. From Figure 1a it is seen that the curve for liquid methanol exhibits the typical behavior of dense fluids. Supporting evidence for this can be considered the fact that its first peak (≈ 1.9) around 3.4 Å is followed by a distinct second and third broad peak located at 4.60 Å and 7.80 Å, respectively. In contrast to this PDF, the COM functions at supercritical conditions show a quite different behavior. For example, a somewhat large reduction in the intensity of the peaks in these PDFs is observed. Note also that the third peak appears to be quite smooth around 8 Å. A more noticeable change occurs in the first and second peaks. The peak positions show a characteristic temperature dependence. This becomes more apparent for the peak amplitudes. Moreover, the short-range part of these functions consists of two overlapping peaks. The first one of them is sharper peaked than the second at temperature and pressure close to the critical point (runs A, B, C). At higher temperatures (runs D–I) this peak is discerned as a “shoulder” on the left side of the second peak, which becomes more apparent in height. Therefore, the first conclusion to be drawn from the COM PDFs is that, over the temperature and pressure range investigated here, the supercritical methanol remains highly structured at relatively short intermolecular distances up to ≈ 5 Å.

To gain deeper insight on the details of the local intermolecular structure of the system, the six site–site PDFs $G_{\text{O-O}}(r)$, $G_{\text{O-H}}(r)$, $G_{\text{H-H}}(r)$, $G_{\text{H-Me}}(r)$, $G_{\text{O-Me}}(r)$, $G_{\text{Me-Me}}(r)$ between the atoms of the methanol molecules have been evaluated. In Figures 2–4 we display the atom–atom PDFs H–H, O–O, and H–O at different temperatures and pressures. MD results of these correlations for liquid methanol are also presented for comparison (see Figures 2a, 3a, and 4a). Note also that these functions are in excellent agreement with those reported by

TABLE 3: Positions and Amplitudes of the First Maximum in the Calculated Pair Distribution Functions PDFs ($r(\text{\AA}):G(r)$) of the Supercritical (runs: A–I) and Liquid Methanol

$G_{\alpha\beta}(r)$	A	B	C	D	E	F	G	H	I	liquid
COM–COM	3.5:1.57	3.5:1.36	3.5:1.31	3.8:1.65	3.8:1.33	3.6:1.24	4.3:1.52	4.3:1.36	4.4:1.35	3.4:1.92
O–O	2.8:2.12	2.8:1.82	2.8:1.80	2.9:1.83	2.9:1.51	2.9:1.42	2.9:1.29	2.9:1.18	2.9:1.13	2.8:3.33
O–H	1.9:1.89	1.9:1.64	1.9:1.63	2.0:1.46	2.0:1.17	2.0:1.17	2.0:0.99	2.0:0.92	2.0:0.87	1.8:3.73
O–Me	3.6:1.68	3.7:1.52	3.6:1.51	3.7:1.68	3.8:1.46	3.9:1.34	3.9:1.45	3.8:1.31	3.8:1.27	3.5:1.99
H–H	2.5:2.15	2.5:1.83	2.5:1.79	2.6:1.86	2.6:1.58	2.5:1.46	2.6:1.36	2.6:1.26	2.6:1.21	2.4:2.93
H–Me	4.1:1.24	4.2:1.14	4.3:1.11	4.1:1.37	4.2:1.20	4.1:1.13	4.1:1.24	4.2:1.13	4.2:1.11	2.8:1.06
Me–Me	4.5:1.76	4.4:1.66	4.4:1.66	4.5:1.83	4.5:1.56	4.4:1.56	4.5:1.64	4.4:1.51	4.5:1.52	4.1:1.98

**Figure 1.** Center of mass pair distribution functions of liquid ((a) $T = 298$ K, $P = 1$ bar) and supercritical (b, c, d) methanol at nine thermodynamic state points: — (523 K); - - (623 K); - · - · (723 K).

Jorgensen^{11c} in a previous Monte Carlo (MC) simulation study of this liquid. From these figures and Table 3 it is obvious that the qualitative trends seen in these PDFs for the liquid are also observed in the corresponding functions at near-critical and supercritical conditions. As shown in Figure 2a–d for example, the H–H curves exhibit only a sharp first peak followed by a minimum at very short interatomic distances. Not only that, but another interesting feature observed is that the position of this peak seems to be slightly affected by temperature and pressure. Thus, over the whole range of investigation its location varies from 2.4 to about 2.6 Å on going from liquid to the extended system. On the other hand, the decrease of the H–H peak height with temperature is more significant. It decreases systematically from the value 2.93 (liquid) to 1.21 in the supercritical thermodynamic state point I, corresponding to 723 K and 300 bar. Furthermore it is interesting to note that at conditions near

the critical point (states A, B, C) the H–H peak intensities remain relatively strong compared to the liquid.

In contrast to the H–H PDFs, the O–O and H–O correlations (Figures 3 and 4) are more structured. The common feature of these functions is the existence of a strongly sharp-peaked first maximum followed by a distinct second maximum, which has to be compared with the first-peak amplitude of the H–H and COM–COM PDFs. At somewhat larger distances these functions exhibit a first deep minimum followed by a distinct second maximum, which indicates the formation of a second solvation shell around the O atom. Note also that the intensity of the second peak in both functions is sufficiently lower than that of the first. Moreover, the temperature and/or pressure dependence of these functions is found to be similar to that obtained for the H–H PDF.

In addition, from the ordering of the first maximum positions r_{ab} ($a, b = \text{O, H, Me, COM}$) of the PDFs (see Table 3), we observe that this correlation distance increases in the following order: $r_{\text{H-O}} < r_{\text{H-H}} < r_{\text{O-O}} < r_{\text{CM-CM}} < r_{\text{O-Me}} < r_{\text{Me-Me}}$. Note also that a somewhat different order of this correlation distance has been obtained in the case of liquid. For example, from Table 3 it is seen that the first maximum of the O–O PDF is located at the same distance, around 2.8 Å, as that of the H–Me function. It may be pointed out therefore that from the overall behavior of the site–site PDFs at liquid as well as at supercritical conditions the methanol molecules in the first solvation shell tend to orient their H atoms toward the O atom, whereas the Me–Me separation was found to be the greatest one compared to the other intermolecular site–site separations. This feature reflects clearly the hydrogen bonded structure between the nearest methanol molecules. This conclusion is confirmed by the hydrogen-bonding analysis presented below.

3.2. Hydrogen Bonding Analysis. As mentioned in the Introduction, our main purpose in the present work is the investigation of the hydrogen bonds between the methanol molecules at supercritical conditions.

From the calculated atom–atom PDFs it is clearly seen that the first solvation shells, specifically in the case of H–O, H–H, and O–O, reflect a pronounced local structure. Moreover, the presence of the first sharp peak in the H–O function at very short correlation distances (1.9–2.0 Å) followed by a deep minimum at an almost unchanged distance (2.6 Å) going from liquid to the supercritical region, may be generally regarded as an indication of hydrogen bonding. In other words, this sharp peak means that a given $\text{H}\cdots\text{O}$ pair exhibits a dimer structure. It may be characterized as a very stable dimer, having a relatively long lifetime at this separation than outside of this. However, in a previous MD study concerning hydrogen bonding in SCW Chialvo and Cummings¹⁵ have shown that the above consideration is not absolutely correct. Concretely, they pointed out that the absence of a first sharp peak in the H–O PDF does not, in general, imply the absence of hydrogen bonding. Therefore, for an accurate estimation of the number of hydrogen

TABLE 4: Average Percentage f_i of Supercritical (runs: A–I) and Liquid Methanol Molecules with i (0,1,2,3,4...) Hydrogen Bonds Together with the Average Total Number of Hydrogen Bonds n_{HB} per Molecule from This Study^a

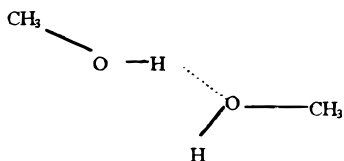
F_i	A	B	C	D	E	F	G	H	I	liquid
0	44.007	33.514	30.673	88.767	67.142	58.244	95.522	79.916	76.295	1.55 (1.8)
1	40.692	43.957	44.357	10.694	28.182	33.933	4.383	18.356	21.334	18.23 (19.0)
2	14.595	21.136	23.282	0.535	4.543	7.541	0.095	1.698	2.317	73.2 (72.9)
3	0.702	1.386	1.678	0.005	0.133	0.281	0.0	0.030	0.054	6.95(6.2)
4	0.003	0.010	0.011	0.0	0.0	0.0	0.0	0.0	0.0	0.016 (0.0)
$2xn_{\text{HB}}$	0.72	0.90	0.96	0.12	0.38	0.50	0.046	0.22	0.26	1.85 (1.84)
n_{HB} [expt]	0.369	0.455	0.497	0.053	0.154	0.233	0.033	0.069	0.105	

^a n_{HB} [expt] is the number of hydrogen bonds per methanol molecule obtained experimentally.¹⁰ Numbers in parentheses are results from a previous Monte Carlo simulation study of this liquid^{11c} on the basis of an energetic criterion.

bonds between different molecules one needs to apply a relevant and rigorous criterion.

Following the literature, various models have been developed for exploring hydrogen bonds of a given type on the basis of energetic and geometric criteria.^{11a,c;16} We can see that these criteria have been employed in CS studies of various dense molecular systems at liquid densities. It is also interesting to mention that water is the only system the hydrogen-bonding structure of which was studied in the framework of these techniques at liquid and also at supercritical (SCW) conditions up to date. Although there have been a number of CS studies of hydrogen-bonding in SCW,¹⁷ only the treatment of Mountain^{17b} and more recently that of Mizan et al.¹⁸ have been systematically extended to incorporate its temperature dependence. Notice, however, that the approach of Mizan et al. is different from that of Mountain in many aspects. For example, Mountain used a rigid water potential model in contrast to a flexible model used by the authors in ref 18. Also, in determining whether a hydrogen-bond exists between a given pair of molecules in the sample, Mountain used a geometric criterion, while the authors in ref 18 applied an energetic one. The quality of this criterion was evaluated by Kalinichev in two previous studies of SCW.^{17a;19} Concretely, Kalinichev seems to favor a combination of an energetic and geometric criterion in order to provide conclusive answers to the problem of hydrogen bonding in SCW.

In the present study we have applied a geometric criterion similar to that used by Klein and co-workers in MD studies of pure liquid methanol and water-methanol, water-acetone liquid mixtures.²⁰ Note also that a similar geometric criterion has been successfully used by Luzar and Chandler²¹ in a more recent MD study of water-DMSO liquid mixtures. Our choice for the above criterion was based upon the behavior obtained for the most relevant of the hydrogen-bonding first peaks of H–O and O–O PDFs at supercritical conditions. It is of course due to the fact that hydrogen bonding involves interatomic configurations of the following type:



As discussed above (recall Figures 3, 4, and 5), the hydrogen-bonding peaks in these functions at supercritical conditions are not diffuse as in the case of the $g_{\text{H-O}}$ for SCW.¹⁸ We mention again that the first minima of these functions are found to be very stable concerning their positions at which they are localized at these conditions. Therefore, a geometric criterion seems to be adequate in the case of the SC methanol. The effectivity, however, of this criterion should be judged from the predicted

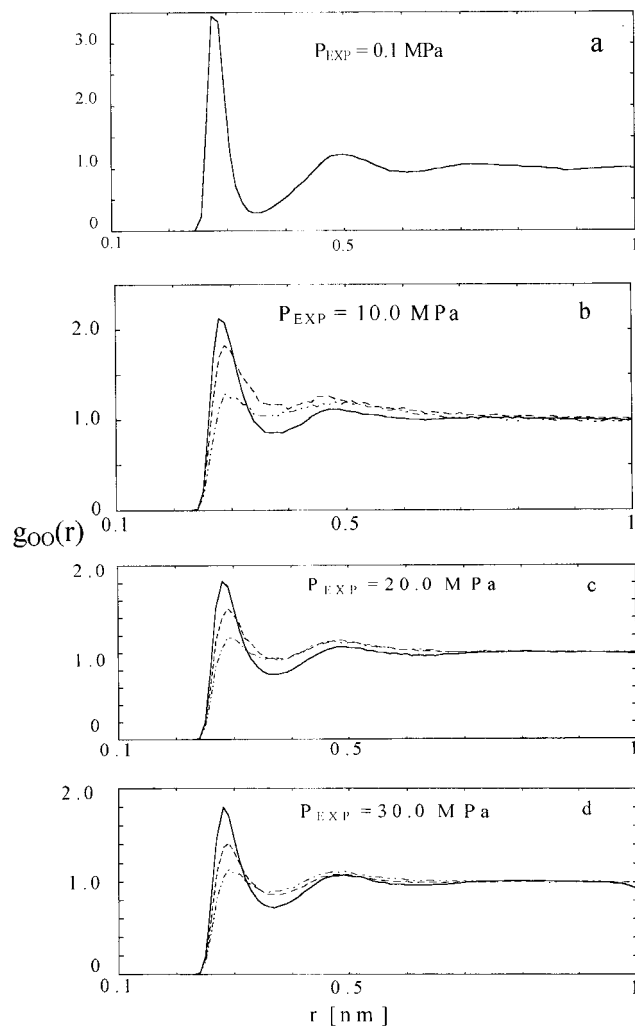


Figure 2. Atom-atom pair distribution functions for O–O of liquid ((a) $T = 298$ K, $P = 1$ bar) and supercritical (b, c, d) methanol at nine thermodynamic state points. The symbols in parts b, c, and d as in Figure 1.

results in comparison with experiment. Thus, a hydrogen bond between two methanol molecules exists if their interatomic separations are such that $R_{\text{O-O}} \leq R_{\text{O-O}}^{\text{C}}$, $R_{\text{H-O}} \leq R_{\text{H-O}}^{\text{C}}$, and the angle H–O–H $\leq \Phi^{\text{C}}$. The cutoff distances $R_{\text{O-O}}^{\text{C}} = 3.50$ Å, $R_{\text{H-O}}^{\text{C}} = 2.60$ Å are taken to be the average distances of the first minimum locations in the $g_{\text{O-O}}$ and $g_{\text{H-O}}$ functions, respectively. To choose the cutoff angle Φ^{C} , we have examined the angular variation of such bonds following the procedure of Luzar and Chandler.²¹ Thus, at each state point, we have systematically estimated the total number of hydrogen bonds in the sample as a function of Φ . The result obtained is that in any case this number does not scale for angles greater than $\Phi = 30^\circ$. Therefore, it is obvious that this angle has been accepted

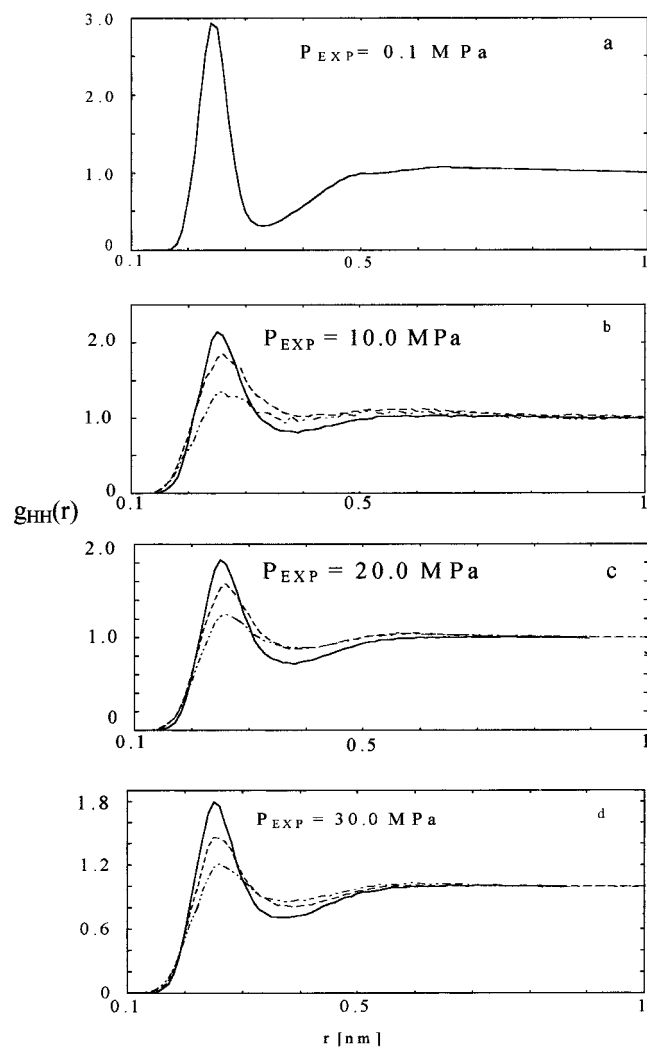


Figure 3. Atom-atom pair distribution functions for H-H of liquid ((a) $T = 298$ K, $P = 1$ bar) and supercritical (b, c, d) methanol at nine thermodynamic state points. The symbols in parts b, c, and d as in Figure 1.

as the cutoff angle Φ^c in our calculations. As we can see, this cutoff Φ^c is the same as that used in MD studies of pure liquid methanol and water-methanol mixtures.²⁰

Before proceeding further, it is interesting to mention here that we have also adopted and examined an energetic criterion proposed by Jorgensen^{11c} in a previous Monte Carlo (MC) simulation study of ambient methanol. According to this criterion, a hydrogen bond is defined by an interaction energy of -12.36 kJ/mol or less suggested by the position of the minima in the obtained energy pair distributions. Jorgensen's MC result for liquid methanol was 1.84 such bonds per methanol molecule. It is interesting to note furthermore that our MD treatment predicts 1.85 hydrogen bonds per methanol molecule with our choice of geometric criterion and 1.84 hydrogen bonds in the case of the energetic one (Table 4). Therefore, our geometric criterion was found to be in quantitative accordance with Jorgensen's energetic one.

In the following, we present and discuss our results. As mentioned above, the quantity of interest is the average number of hydrogen bonds per methanol molecule n_{HB} at each state point of interest. However, our calculations are extended to incorporate hydrogen-bond statistics by estimating the percentage distribution f_i of molecules with i ($i = 0, 1, 2, \dots$) bonds per molecule.

In Table 4, we summarized all these results together with experimental predictions reported by (HC).¹⁰ In the same table,

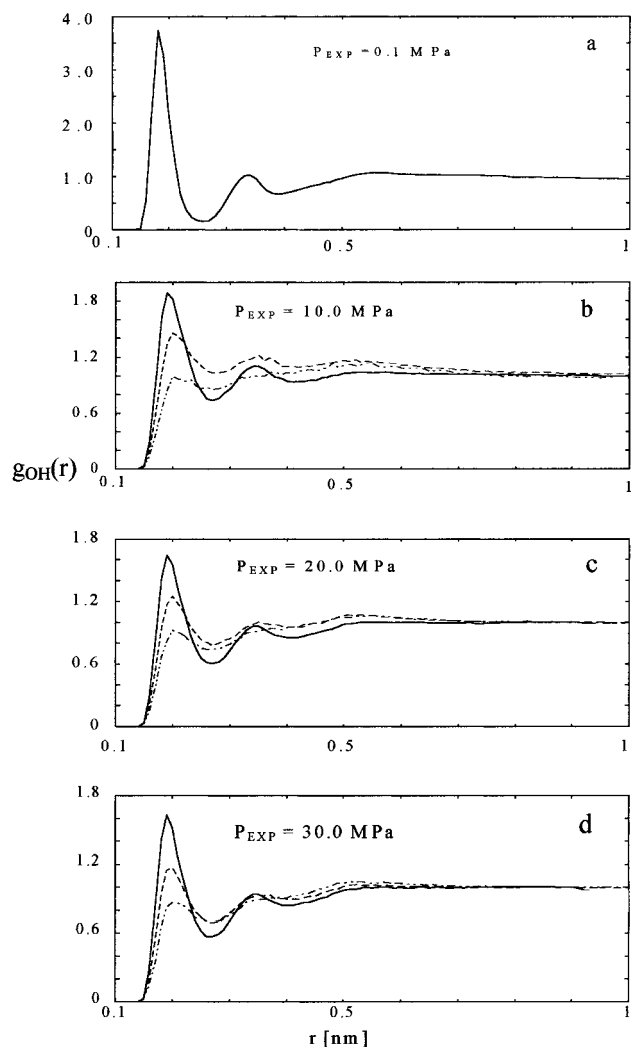


Figure 4. Atom-atom pair distribution functions for H-O of liquid ((a) $T = 298$ K, $P = 1$ bar) and supercritical (b, c, d) methanol at nine thermodynamic state points. The symbols in parts b, c, and d as in Figure 1.

we also present results for the liquid methanol at 298 K from the present MD study. As noted in ref 10, the degree of hydrogen bonding of supercritical methanol n can be read directly from the right-hand axes in Figure 3, reported in this paper. However, for our purpose these data have been reproduced here by using eq 1 in their paper and the original methanol chemical-shift measurements σ at these conditions obtained from the authors.²²

As pointed out by these authors, the degree of hydrogen bonding present in supercritical alcohols is "linearly" related to the obtained chemical shift σ . Moreover, in the case of supercritical methanol, the proposed linear relation is given by

$$n = 0.202\sigma + 0.687 \quad (2)$$

where σ is the observed chemical shift of the hydroxyl protons relative to the methyl resonance.

The average number of hydrogen bonds per molecule from the present simulation and from experiment are also depicted in Figure 5 as a function of pressure and for 250, 350, and 450 °C.

As we can see from Table 4 and Figure 5, the agreement between simulation and experiment is excellent. Also, the temperature and pressure dependence of this quantity from the experiment was found to be very similar to that of simulation. As in the case of hydrogen bonding in SCW,¹⁸ the decrease of

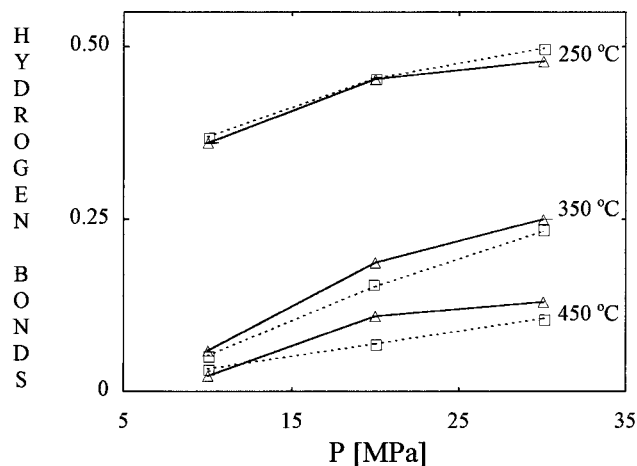


Figure 5. The number of hydrogen bonds n_{HB} as a function of pressure and temperature: — (expt),¹⁰ - - - (MD this work).

the hydrogen bonds in supercritical methanol is primarily temperature dependent. In addition, by inspecting the results obtained for the hydrogen-bond statistics we may conclude that supercritical methanol mainly forms one hydrogen bond per molecule. Also, our calculations provide a significant percentage of monomers ($i = 0$), as well some percentage of molecules in two hydrogen bonds ($i = 2$). On the other hand, the statistics for liquid methanol show that the most significant percentage (73.2%) of molecules appears with two hydrogen bonds per molecule. Moreover, the percentages of molecules obtained for $i = 1$ (18.23%) and $i = 3$ (6.95%) are found to be also significant.

4. Summary and Conclusions

In the present paper, a molecular dynamics simulation study of supercritical and liquid methanol has been performed in order to study the hydrogen-bonding structure of the fluid. The system has been investigated at nine thermodynamic state points, for which experimental data are available. The temperature ranged from 523 to 723 K at densities corresponding to experimental pressures from 100 to 300 bar. The liquid was simulated at 298 K and normal pressure.

The hydrogen-bond network at each state point has been studied on the basis of a well-defined geometric criterion. Also, hydrogen-bond statistics have been evaluated. The main result is that hydrogen bonding is still present in supercritical methanol. This conclusion is in accord with the previous findings of Hoffmann and Conradi from NMR chemical shift measurements. Also, the average total number of hydrogen bonds per molecule is obtained and compared with available experimental data. We find that over the whole range of investigation the agreement between experiment and simulation is excellent.

From the hydrogen-bonding statistics we may conclude that supercritical methanol molecules form mainly one hydrogen bond per molecule, while liquid methanol molecules form mainly two hydrogen bonds per molecule.

Finally, further investigations are clearly needed to determine the hydrogen-bonding dynamics and clustering in supercritical methanol. Work on this area is in progress.

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