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Translational and rotational dynamics in supercritical methanol from molecular dynamics simulation*

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Abstract: The purpose of this paper is to review our latest molecular dynamics (MD) simulation studies on the temperature and density dependence of the translational and reorientational motion in supercritical (SC) methanol. In the present treatment, Jorgensen's [W. L. Jorgensen. *J. Phys. Chem. A* **102**, 8641 (1998)] transferable potential model, tested in a recent MD study of hydrogen bonds in this fluid [M. Chalaris and J. Samios. *J. Phys. Chem. B* **103**, 1161 (1999)], was employed to simulate the dynamics of the system. The simulations were performed in the canonical (NVT) ensemble along the isotherms 523, 623, and 723 K and densities corresponding to the pressures from 10 to 30 MPa. Several dynamical properties of the fluid have been obtained and analyzed in terms of appropriate time-correlation functions (CFs). With respect to the translational dynamics, the self-diffusion coefficients obtained have been used to test the applicability of the well-known Chapman–Enskog kinetic theory. We have found that the theoretical predictions for the self-diffusion coefficients are only in qualitative agreement with the MD results over the whole temperature and density range studied. Finally, the inspection of the reorientational CFs and their corresponding correlation times lead to the conclusion that the reorientational motion of the SC methanol molecules in the sample is anisotropic.

INTRODUCTION

In recent years, supercritical fluids (SCFs) have stimulated much academic and technological interest [1,2]. This interest is due to the fundamental questions of their unique physicochemical properties as far as to their considerable practical importance. Note that the density of a SCF in the near-critical region can be varied continuously and markedly from liquid- to gas-like values even by a relatively small variation in pressure or temperature. This characteristic feature makes SCFs attractive alternatives to liquid solvents for a number of chemical processes. As it becomes apparent from earlier studies, however, a deeper and quantitative understanding of the pressure and temperature dependence of these noticeable density fluctuations and their influence on the structural and dynamic properties of these systems has not yet been achieved. Several views of the microstructure and dynamics of SCFs are far from being substantial. On the other hand, the microscopically based understanding of the properties of supercritical (SC) solvents is indispensable for a more efficient use of these systems as media for a variety of chemical, analytical, and industrial applications. Thus, systematic studies of SCFs based on standard experimental and theoretical techniques are clearly needed to explore the behavior of their properties as well as to evaluate their usefulness for further development of industrial applications.

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Among many polar organic compounds widely used as cosolvents in industrial processes, is certainly methanol (MeOH), ethanol (EtOH), and 2-propanol [2]. Moreover, alcohols could be alternatives to water as solvents at SC conditions for a number of reasons. Therefore, investigating pure alcohols and alcohol mixtures at liquid and SC conditions is of particular interest. As far as we know, however, there are only a few experimental and theoretical investigations of the properties of pure alcohols in the SC state available in the literature and numerous questions about the behavior of these fluids still remain unanswered. On the other hand, the importance of exploring the intermolecular interactions in SC fluids and especially in SC water and alcohols [3–5] has been recognized over the last decade. We mention that the effect of temperature and pressure on the hydrogen-bond structure of some liquid alcohols has been investigated by means of various spectroscopic and computer simulation (CS) techniques [6,7]. Furthermore, following the literature we can notice that such studies on SC alcohols are unfortunately scarce.

As a part of our CS studies on SC fluids, we have recently reported a MD simulation study of the hydrogen-bonding structure of SC and liquid MeOH [8]. In that paper, the hydrogen bonds in the fluid were studied on the basis of a well-defined hydrogen-bonding criterion. Also, the average number of hydrogen bonds per molecule was obtained and compared with available data from NMR chemical shift measurements reported in a previous study by Hoffman and Conradi (HC) [9]. Note that HC studied the hydrogen bonding in SC MeOH and EtOH up to 450 °C and over a wide range of pressure up to 350 bar. The main result obtained from our previous study is that hydrogen bonding is still present in SC methanol and the molecules remain highly structured. In addition, the calculated average numbers of hydrogen bonds per molecule are found to be in quantitative agreement with corresponding available data from NMR measurements [9].

In a recent work on this area of investigation, Asahi and Nakamura (AN) [10] reported NMR and MD results for MeOH up to the supercritical region. They made a chemical shift study of MeOH from 289 to 580 K and at reduced densities ρ_r ($\rho_r = \rho/\rho_c$, $\rho_c = 272$ kg m^{-3}) between 0.183 and 1.008. Note that their MD simulations were performed at the same thermodynamic conditions. They concluded that the experimental self-diffusion coefficients observed in the SC region are in good agreement with those calculated from MD simulations and via the Chapman–Enskog (CE) kinetic theory. In addition, their MD simulations have shown that hydrogen-bonded clusters of MeOH are chain-like and the number of molecules in the clusters decreases with increasing temperature and decreasing density.

Most recently, Yamaguchi et al. [11] reported a neutron diffraction (ND) study of SC MeOH. They suggested that clusters of 3–5 molecules exist in SC MeOH at moderate densities. In addition, SC MeOH was investigated experimentally via FT–IR, Raman, UV–vis, NMR, as well as dielectric (DR) relaxation techniques [12–16]. Nevertheless, CS studies concerning the translational and reorientational dynamics of this fluid have not been reported so far. As mentioned above, self-diffusion coefficients of the molecules in SC MeOH have been reported by AN [10] and by us in our first MD treatment of this fluid. Thus, although we have some information about the temperature and pressure dependence of the translational diffusion of this fluid, it appears that we do not have a broad quantitative knowledge regarding its overall dynamics. In other words, our knowledge about the dynamics of the system is quite restricted. The influence of the hydrogen bonds, for instance, on the static and dynamical properties of the fluid is clearly not well understood, and further investigations are needed to determine the detailed nature of their behavior.

In this MD study, we will focus our attention to the dynamics of the MeOH molecules up to the supercritical region, by investigating the behavior of the single-molecule translational and rotational motion in a wide range of temperature and pressure. The translational and rotational dynamics of the molecules have been studied in terms of appropriate time-correlation functions (CFs), which have been calculated, analyzed, and compared with corresponding theoretical model functions.

COMPUTER SIMULATION DETAILS

The MD simulations were performed in the canonical (NVT) ensemble with 256 methanol molecules in a cubic box using periodic boundary conditions. The analytical description of the potential model used and the fundamental technical details applied in the simulation have been described in earlier treatments [8,17]. The system was simulated at various SC thermodynamic points summarized in Table 1. We must note that after equilibration each MD run was extended up to 250 ps with an integration time step of 2.5 fs.

Table 1 The simulated state points (T, ρ, P) of SC MeOH in this study. Depicted are the bulk thermodynamic properties and the self-diffusion coefficients obtained from this work and on the basis of the Chapman–Enskog [18,19] kinetic theory derived for the LJ fluid of the SC MeOH.

	Experimental			Simulation			Theory
Therm. states	T (K)	ρ (g·cm^{-3})	P (MPa)	T (K)	P (MPa)	D (10^{-9} m^2 s^{-1})	D (10^{-9} m^2 s^{-1})
A	523	0.348	10.0	522.6	11.5	60.95	73.00
B	523	0.516	20.0	522.4	29.2	34.57	49.23
C	523	0.563	30.0	522.4	46.1	27.90	45.12
D	623	0.070	10.0	623.4	9.4	380.0	431.93
E	623	0.260	20.0	623.0	24.8	98.50	116.29
F	623	0.365	30.0	622.1	36.3	64.80	82.84
G	723	0.040	10.0	723.6	6.9	788.0	871.58
H	723	0.200	20.0	723.3	30.1	150.0	174.31
I	723	0.250	30.0	723.3	37.6	118.0	139.45

Several properties of this model, including the system bulk thermodynamics and structure, as well as transport and hydrogen-bonding predictions, have been presented and discussed in ref. [8]. As mentioned in the Introduction, the main objective of the present work is to explore the temperature and pressure dependence of the single molecule dynamical properties of SC MeOH. Therefore, the present study may be regarded as an extension of our first treatment on this SC fluid.

The estimated errors were maximal: ±3 K for the temperature and ±12 % for the pressure.

RESULTS AND DISCUSSION

Translational motion

The calculated bulk thermodynamic properties of the system at thermodynamic state points of interest are found to be reasonable compared with corresponding experimental data. On the other hand, there are two methods to calculate the self-diffusion coefficients of the molecules from MD trajectories. The first way is via integration of the linear-velocity CFs and the second one is that of the mean-square displacement of the molecules via the well-known Einstein relation. In this work, we have used both methods and the results obtained are found almost identical. The results obtained on the basis of the Einstein relation are shown in Table 1. From this table, it is clearly seen that the self-diffusion coefficients show a marked decrease with decreasing temperature at constant pressure. Also, they decrease with increasing pressure at constant temperature. Unfortunately, a direct comparison of our predicted diffusion data with experiment is not feasible since experimental self-diffusion coefficients for this system at SC conditions of our interest are not available so far. We recall here that the authors AN in ref. [10] investigated the temperature and density or pressure dependence of the self-diffusion coefficients of MeOH ranging from 289 to 580 K and from 0.049 to 0.274 g/cm^3. These thermodynamic state points of MeOH

are ranged near and above its critical temperature (T_c = 513 K), but they are sufficiently different to those investigated experimentally by HC in ref. [9].

To gain deeper insight on the details of the diffusivity of SC MeOH, one needs to explore a number of possible factors that might affect the translational motion of the molecules in the fluid at these conditions. However, it is realistic to assume that a possible explanation of such a variation of the diffusion coefficients with temperature at constant pressure is relied to the existence of some kind of dynamical hydrogen-bonding network or a temperature-dependent local fluctuated aggregation formed by a number of molecules. This consideration is confirmed by the hydrogen-bonding analysis presented in recent experimental and computational studies of SC MeOH.

Before proceeding any further, it is of particular interest to compare and discussed our MD diffusion data for SC MeOH with results obtained theoretically. We mention here that the authors in ref. [10] pointed out that the temperature and pressure or density dependence of the self-diffusion coefficient of SC MeOH may be discussed on the basis of the well-known Chapman–Enskog (CE) kinetic theory for Lennard–Jones (LJ) fluids [18,19]. Concretely, they found that the experimental results obtained for the self-diffusion coefficients of MeOH in the aforementioned SC region are in good agreement with those calculated using the CE theory. They also concluded that their experimental self-diffusion coefficients are in excellent agreement with MD results over the whole temperature and density range studied. Taking into account the former concluded remark of the authors AN, we decided to employ the same kinetic theory to obtain theoretical self-diffusion coefficients for SC MeOH. In a first approximation, the CE diffusion equation derived for LJ fluids is given by

$$D = \frac{3\left(\pi K_B T / m\right)^{1/2}}{8\pi n \sigma^2 \Omega^{(1,1)^*}\left(T^*\right)}, \tag{1}$$

where m and n are the molecular mass and number density of the system, respectively. K_B is the Boltzmann constant and T^* is the reduced temperature expressed as $T^* = K_B/\varepsilon$. ε and σ are the LJ potential parameters for MeOH interactions taken from ref. [18]. The collision integrals $\Omega^{(1,1)^*}$ (T^*) are taken from Table IV in ref. [19].

The self-diffusion coefficients for MeOH at the above-mentioned SC conditions and from the CE theory are also depicted in Table 1. From this table, it is clearly seen that the theoretically predicted diffusion coefficients are only in semi-quantitative agreement with those from the simulation. It is therefore evident that more accurate theory must be employed to approximate the simulated diffusion data of SC MeOH at the conditions studied by HC and by us in the present treatment.

In this work, we have studied the translational motion of the SC MeOH molecules at each thermodynamic state of interest and in terms of the calculated center-of-mass (COM) linear velocity autocorrelation functions (vACFs), $C_V(t)$. These correlations are shown in Fig. 1. From the plots in this figure, we may observe that the $C_V(t)$ ACFs decay faster as the density increases by increasing pressure or decreasing temperature and that in the density range under study they do not exhibit a negative part. The correlation times for the linear velocity ACFs are selected in Table 3.

Although the $C_V(t)$ curves in Fig. 1 seem to decay exponentially, however, by using a careful nonlinear least-squares fit procedure, we fund that a model function that adequately reproduces the MD $C_V(t)$ ACFs is given by the following form:

$$C_V(t) = (1-c)\cdot\left(1+\frac{t}{\tau_1}\right)e^{-\frac{t}{\tau_1}} + c\left(1+\frac{t}{\tau_2}\right)e^{-\frac{t}{\tau_2}} \tag{2}$$

The simulated and adjusted vACFs are displayed in Fig. 1. The values for the parameters c, τ_1, and τ_2 of eq. 2, are summarized in Table 2.

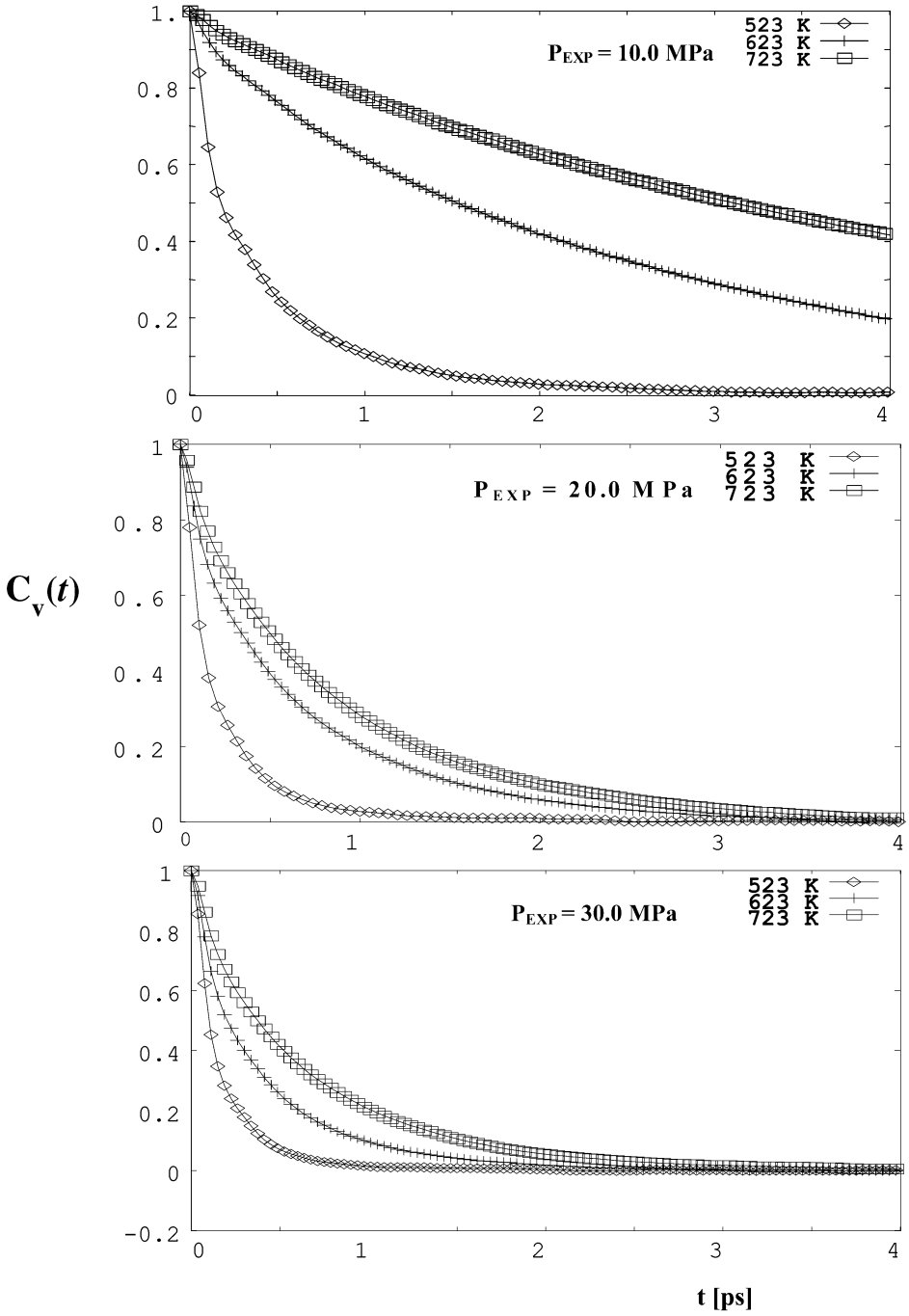


Fig. 1 The center-of-mass linear velocity ACFs $C_V(t)$ obtained from this study and the corresponding model functions. The symbols correspond to the MD results and the solid lines to the model function.

Table 2 Parameter values for the model function from eq. 2 for the linear velocity and angular momentum ACFs obtained from this study of SC MeOH.

RUN	$C_V(t)$			$C_J(t)$		
	C	τ_1	τ_2	c	τ_1	τ_2
A	0.42828	0.055038	0.379997	0.167041	0.042144	0.235566
B	0.356919	0.439345	0.212891	0.029807	0.037794	0.242802
C	0.331629	0.042117	0.179262	0.004303	0.036039	0.510010
D	0.364593	1.69631	0.253181	0.427357	1.03165	0.131579
E	0.478585	0.500917	0.075024	0.693603	0.196493	0.045665
F	0.533422	0.337638	0.059144	0.359131	1.89968	0.300645
G	0.340114	3.18484	0.529877	0.359193	1.89968	0.300645
H	0.422416	0.612102	0.100447	0.505026	0.390865	0.069541
I	0.448579	0.488247	0.083059	0.527184	0.301414	0.059394

The time evaluation of the total force field acting on each molecule in the sample was studied by calculating the COM total force ACFs, $C_F(t)$. Figure 2 shows the shapes for these correlations from which it is clearly seen that the $C_F(t)$ ACFs decay faster than the corresponding $C_V(t)$ functions. Note that the $C_F(t)$ ACFs exhibit a negative portion. This means that on average the total force acting on each MeOH molecule from the surrounding cage molecules changes direction more frequently (at relatively very short time intervals) than the linear velocity of the molecule. This implies that the translational motion of MeOH molecules remains somewhat restricted at these SC conditions. This feature is supported by the results obtained from local intermolecular structure and hydrogen-bonding analysis of this system reported in recent studies. We mention that our recent calculations reveal that over the temperature and pressure range studied the MeOH molecules remain highly structured. Finally, we have found that a theoretical function given by eq. 3 can approximate the simulated MD $C_F(t)$ ACFs of this system quite successfully.

$$C_F(t) = \frac{3mKT}{\langle F^2 \rangle}\left(\frac{c \cdot e^{-\frac{t}{\tau_1}}}{\tau_1^2}\left[1 - \frac{t}{\tau_1}\right] + \frac{(1-c)\cdot e^{-\frac{t}{\tau_2}}}{\tau_2^2}\left[1 - \frac{t}{\tau_2}\right]\right) \tag{3}$$

The mean-square force $\langle F^2 \rangle$ and torque $\langle T^2 \rangle$ acting on each MeOH molecule due to its surrounding molecules are calculated and the results obtained are selected in Table 3. Moreover, a linear density dependence of these quantities is obtained. Specifically, we may observe that the mean-square torque $\langle T^2 \rangle$ behaves linearly with density and it approaches zero at very low densities, as expected.

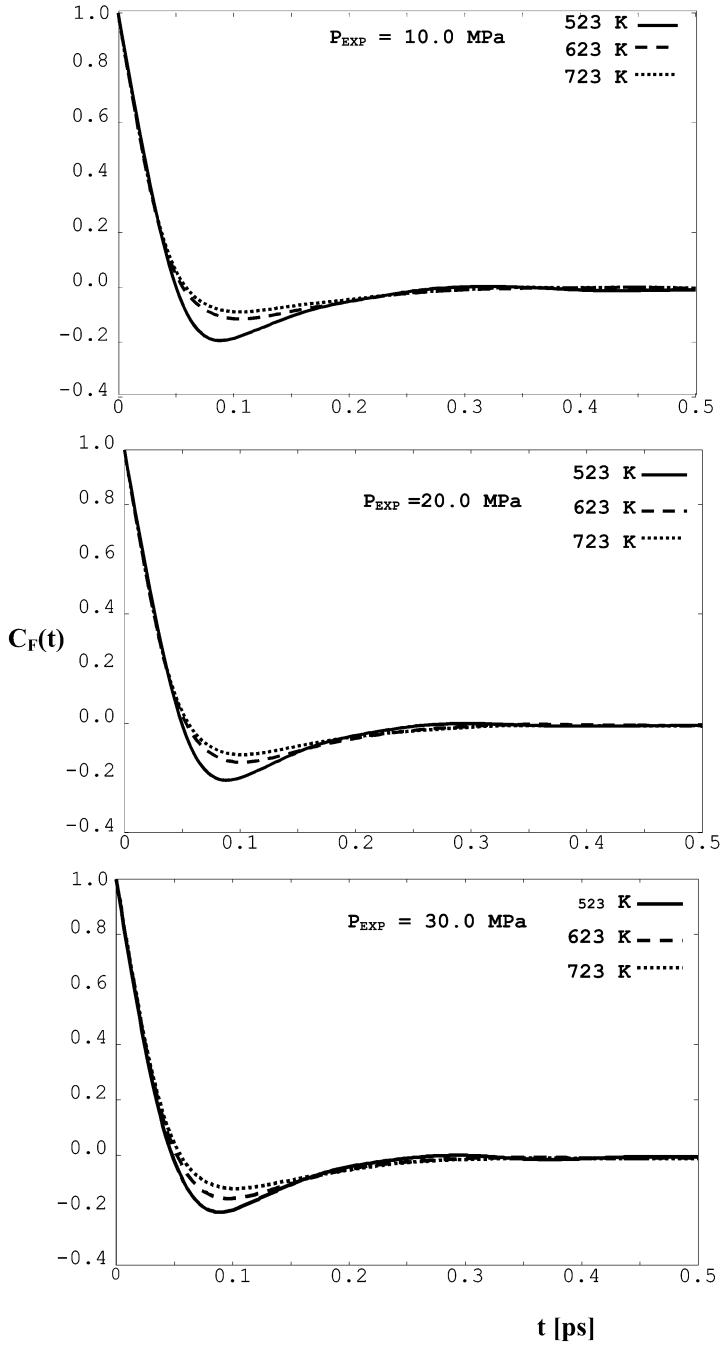


Fig. 2 The force ACFs $C_F(t)$ obtained from this MD simulation study.

Table 3 Correlation times τ_C (ps) of the linear velocity v, angular momentum J, P_1 and P_2 Legendre polynomials, system total dipole moment **M**, ACFs as well as the mean-square force $\langle \boldsymbol{F}^2 \rangle$ (10^{-18} N^2) and torque $\langle \boldsymbol{T}^2 \rangle$ [10^{-20} $(Nnm)^2$] values obtained from this study.

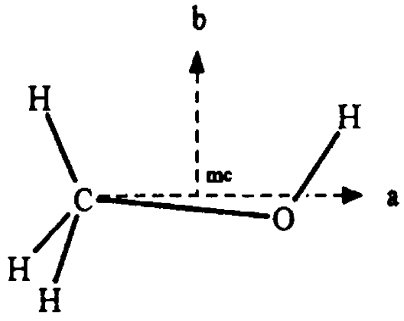
MD	$\langle F^2 \rangle$	$\langle T^2 \rangle$	τ_v	τ_J	τ_{1c}	τ_{1b}	τ_{2c}	τ_{2b}	τ_D
A	0.205	0.178	0.453	0.180	0.352	0.203	0.111	0.084	0.590
B	0.280	0.229	0.257	0.120	0.431	0.250	0.142	0.108	0.910
C	0.306	0.244	0.207	0.097	0.473	0.271	0.168	0.108	0.997
D	0.047	0.040	2.40	1.333	0.083	0.066	0.042	0.035	0.102
E	0.152	0.123	0.615	0.298	0.150	0.099	0.061	0.053	0.288
F	0.207	0.162	0.405	0.211	0.191	0.112	0.071	0.060	0.331
G	0.024	0.019	4.835	2.86	0.067	0.057	0.034	0.032	0.028
H	0.120	0.090	0.812	0.477	0.106	0.070	0.042	0.050	0.154
I	0.148	0.109	0.636	0.364	0.107	0.075	0.045	0.047	0.085
Liq.	0.314	0.277	0.050	0.023	6.34	3.36	2.01	1.15	21.96

Rotational motion

The analysis of the rotational dynamics of the SC MeOH is based on the most common ACFs, namely, the angular momentum ACF, $C_J(t)$ and the first- and second-order Legendre reorientational ACFs, $C_L(t)$, of the unit vectors along the principal rotational axis c and b of the molecule:

$$C_L^x(t) = \left\langle P_L\left[\hat{\boldsymbol{u}}_x(0)\cdot\hat{\boldsymbol{u}}_x(t)\right]\right\rangle, x = c, b;\ L = 1, 2. \tag{4}$$

$\hat{\boldsymbol{u}}_c$ and $\hat{\boldsymbol{u}}_b$ represents the unit vectors along the principal rotational axis c and b of the molecule, respectively. Legendre correlations for the unit vector $\hat{\boldsymbol{u}}_a$ along the third principal rotational axis a of the molecule have not been investigated. Note that the moment of inertia for the principal axis a (I_a = 0.00737 amu·nm^2) is too small in comparison with that of b (I_b = 0.16732 amu·nm^2) and c (I_c = 0.17468 amu·nm^2). In the following schematic representation, the axis c is perpendicular to the ab plane and mc denotes the mass center of the MeOH molecule.



The angular momentum ACFs $C_J(t)$ are shown in Fig. 3. From this figure, one notices that these ACFs display a similar behavior in comparison to that of the $C_V(t)$ ACFs. In other words, these ACFs decay faster as the density increases and they do not exhibit a negative (anticorrelation) part. This means that the angular momentum does not describe large alterations of its direction. As in the case of the $C_V(t)$ ACFs, we fitted eq. 2 to the simulated $C_J(t)$ ACFs points and found that this procedure was also successful. The obtained parameter values are given in Table 2, and the corresponding correlation times are selected in Table 3.

The Legendre ACFs $C_1^c(t)$, $C_1^b(t)$, $C_2^c(t)$, and $C_2^b(t)$ are not shown here as they exhibit typical behavior. They remain positive and converge to zero approximately after 3 ps. Also, the results reveal

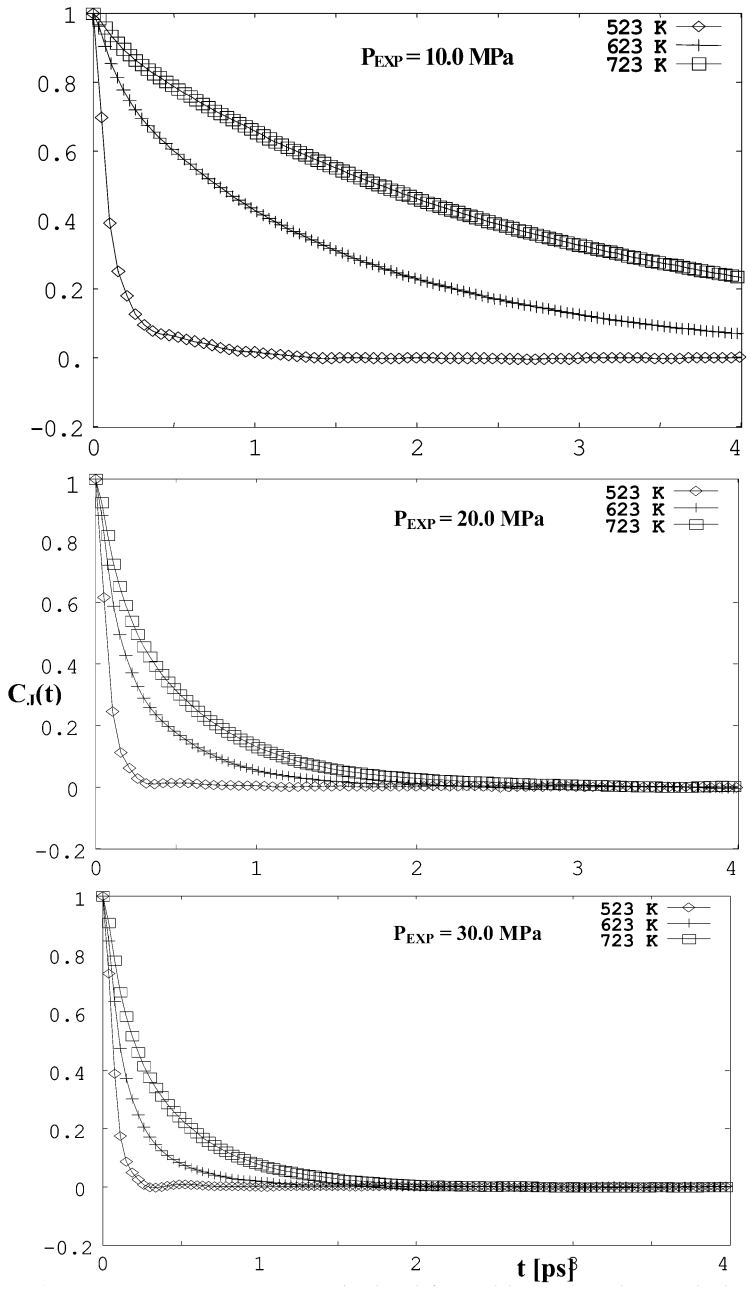


Fig. 3 The angular momentum ACFs $C_J(t)$ obtained from this study. The symbols represent the MD results and the solid lines the model function of eq. 2.

characteristic density dependence. The single molecule reorientational correlation times τ_L^x (L = 1, 2; $x = b, c$) have been obtained by integrating the ACFs up to 6 ps and they are presented in Table 3. By inspecting the predicted correlation times, τ_L^x, we observe that in all cases the correlation times τ_1^c and τ_2^c are found to be greater than the corresponding times τ_1^b and τ_2^b, as expected. Such a feature may be easily explained in terms of the moments of inertia corresponding to the b, c principal axes of the molecule.

In all cases, the correlation times, τ_L^x, decrease by increasing pressure at constant temperature. This result is consistent with the hydrogen-bonding behavior of the fluid. Also, our predictions reveal that the reorientational motion of the species in the sample is anisotropic. Furthermore, we found that the MD correlation times for $L = 2$ are in quite reasonable agreement with available experimental results reported by Bai and York (BY). Note that the latter authors studied SC MeOH using capillary high-pressure NMR spectroscopy [16].

Another important and closely related aspect to the rotational motion of the SC methanol molecules concerns the extent over which the temperature or density affects the reorientational diffusion motion of the molecules. The calculated correlation times and the time evolution of the reorientational ACFs show a moderate pressure dependence in addition to temperature weak effects on this molecular motion. Our conclusions concerning this problem will be presented in a forthcoming publication.

CONCLUSIONS

In this paper, we have reported results from our latest MD simulation studies of SC MeOH at temperatures from 523 to 723 K and densities corresponding to experimental pressures from 100 to 300 bar. The main purpose of our study was to investigate the single molecular dynamical properties of the fluid. This was achieved by exploring the single-molecule translational and reorientational dynamics of the system in terms of the appropriate ACFs with temperature and/or pressure or density. These ACFs were calculated, analyzed, and discussed. On the basis of present and previously reported results, we may conclude that the rearrangement of hydrogen bonds in the fluid affect significantly the translational and reorientational motion of the MeOH molecules at these SC conditions. We found that the simulated self-diffusion coefficients of the fluid are in semi-quantitative agreement with results from the Chapman–Enskog kinetic theory. The calculated second-order Legendre reorientational correlation times of the molecules in the sample are found to be in quite good agreement with recent NMR data. Finally, the calculated reorientational ACFs reveal that the reorientational motion of the molecules is anisotropic.

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