

Local intermolecular structure and dynamics in binary supercritical solutions. A molecular dynamics simulation study of methane in carbon dioxide

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Abstract

The binary supercritical mixture methane–carbon dioxide (SC CH₄–CO₂) with mole fraction of methane $X=0.2$ was investigated at temperature $T=323.15$ K and density $\rho=0.23814$ g/cm³ corresponding to a pressure 9.94 MPa, by using the molecular dynamics (MD) simulation technique in the canonical (NVT) ensemble. The local intermolecular structure of the fluid was investigated in terms of the appropriate pair radial distribution functions, which have been calculated and analyzed. The estimated average local coordination numbers and mole fractions around the species in the mixture have been used to explore the repulsive or attractive nature of the fluid. The results obtained have led to the conclusion that the SC CH₄–CO₂ mixture at these conditions might be characterized as a repulsive one. This result supports the conclusions of a previously reported experimental work by Baglin et al. [F.G. Baglin, S.K. Murray, J.E. Daugherty, T.E. Palmer, W. Stanbery, Mol. Phys. 98 (2000) 409.]. The single reorientational dynamics of both the solute and solvent species in the mixture were also investigated by calculating the appropriate time correlation functions. The observed time dependence of these functions are discussed in relation with the local environment around the species, which in the case of the solute molecules seems to be strongly affected.

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1. Introduction

In recent years, numerous experimental as well as theoretical investigations have been devoted to study the properties of supercritical (SC) solvents. This research remains a very active area of interest for many reasons. The efficiency, for instance, of some SC fluids (SCFs) for replacing toxic industrial solvents, and their ability to exhibit a catalytic role in the evolution of important chemical processes at mild conditions, such as fluid extraction, chromatography, chemical synthesis and analysis underlies this particular interest [1–3]. Furthermore, one of the most important characteristics of SCFs is that their properties can be drastically changed from gas-like to liquid-like values with small changes of some thermodynamic variables, especially in the critical region. For example, small changes in the pressure of SCFs can cause significant differences in their density, because of their high compressibility value. Due to that fact, their dissolving capability could

be tuned through such kind of small changes in the thermodynamic parameters, allowing the selective solvation of different types of solutes. These features make SCFs attractive alternatives to liquid solvents for use in the developments of new chemical processes [4].

One of the possible origins of this peculiar behavior of SCFs' properties is the existence of local density inhomogeneities. It has been pointed out that the compressibility of a fluid is directly related to the range over which microscopic fluctuations in density are correlated. As a result of this, the overall picture of a SCF in its compressible regime is that of an inhomogeneous medium with high and low-density regions (small cluster and molecular aggregates). In general, previously reported studies in the literature have led to the conclusion that undoubtedly local density inhomogeneities are real and important phenomena in compressible SCFs [5–29]. Furthermore, a thermodynamic state-point dependence of the extent of these fluctuations from mesoscopic to microscopic length-scale has been observed; this causes corresponding changes in solute solvation and reaction dynamics. However, a deeper and more quantitative understanding on the state-point dependence of the local density fluctuations and

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Table 1
Thermodynamic results for the binary SC system methane–carbon dioxide from this MD study

$T=323.15$ K	
$-U_{\text{pot}}$ (kJ mol $^{-1}$)	2.628 (± 0.086)
P (MPa)	11.220 (± 2.140)
E (kJ mol $^{-1}$)	4.349 (± 0.197)
$\langle F^2 \rangle$ (10^{-18} N 2)	0.025 (± 0.006)
$\langle \Gamma^2 \rangle$ (10^{-38} N 2 m 2)	0.021 (± 0.005)

Error bars are indicated in the parentheses.

their effects on SCF's properties, as well as on the determination of the factors which control the range of thermodynamic conditions over which density enhancements are important, has not yet been achieved.

Although several theoretical and experimental investigations have been devoted to the investigation of the nature of local solvent density inhomogeneities in infinitely dilute SC solutions, questions concerning the solvation processes in binary SC mixtures with greater solute concentrations have not yet been definitively answered.

SC carbon dioxide and methane are the most applicable fluids in the aforementioned chemical and industrial processes, as well as in fossil fuel technology and geosciences. Furthermore, of particular academic and industrial interest in this area of research is the storage of these fluids in adequate amounts into suitable nanoporous materials [30–36]. However, the behavior of their binary mixtures has not been extensively investigated.

According to previously reported experimental investigations, Baglin et al. [37] have employed interaction induced Raman light scattering techniques (iiRLS), in combination with theoretical calculations using the Ornstein–Zernike integral equation (OZIE) method to investigate the local density structure of the binary mixture methane–carbon dioxide (with methane as the solute – 10% mol concentration). In that treatment, they have used the OZIE analytical theory to predict and compare the solute–solvent and solvent–solvent local coordination numbers and then to correlate theoretical results with that from their iiRLS measurements, which provide information for the solute–solvent interactions in the mixture. According to the concluded remarks reported in Baglin et al. [37], the methane–carbon dioxide system has been identified as a repulsive (avoidance) one.

To the best of our knowledge, computer simulation studies on the aforementioned fluid mixture have not been reported so far. Thus, we have decided to extend these previous investigations in order to study the behavior of the mixture at slightly larger methane concentrations and, of course, to explore the influence of the solute concentration on the density micro-heterogeneities of the system.

In this study we present the first part of our treatment devoted to the investigation of the binary supercritical mixture methane–carbon dioxide with corresponding mole fractions 0.2 and 0.8, at $T=323.15$ K and $\rho=0.23814$ g/cm 3 [38] by employing the molecular dynamics (NVT-MD) simulation technique. In the framework of this study, the local structure

around the solute and solvent molecules was investigated in terms of the appropriate radial pair distribution functions (RPDFs). The average local mole fractions around both species (solute and solvent) were also estimated and the results obtained were presented and discussed. In addition, the single-particle reorientational dynamics of the molecules were also studied.

The remainder of the paper is organized as follows. The potential models and computational details are described in Section 2 while our results and concluding remarks are presented in Sections 3 and 4, respectively.

2. Computational details and potential models

The interaction potentials employed in this study to model methane and carbon dioxide were the rigid OPLS-AA and EPM2, respectively. According to our previous simulation studies, these models have been found to be quite reliable in predicting the properties of the pure SC fluids as well as the properties of the CO $_2$ –methanol binary mixture [27,39,40]. Thus, these previously reported results led us to select and employ these potentials in our present investigation. The OPLS-AA model is a five-site LJ 12-6 potential plus coulombic terms, whereas the EPM2 one is a three-site model with the same functional form. The cross interactions were calculated by using the Lorentz–Berthelot combining rules. A complete description of these potential models is given in Refs. [39,40].

At the SC condition under investigation ($T=323.15$ K, $P=9.94$ MPa, $\rho=0.23814$ g/cm 3) [38], we performed a simulation for a system consisting of 100 methane and 400 carbon dioxide molecules in the central simulation box using periodic boundary conditions. A spherical cutoff with half the box length as the cutoff distance was used to truncate the short-range interaction. The well-established Ewald summation method was utilized to account for the long-range electrostatic corrections. Molecular orientations have been formulated by the implementation of the quaternion formalism and the translational and rotational equations of motion were integrated using the leapfrog algorithm. In the present treatment, the integration time step used was 1 fs. The initial configuration

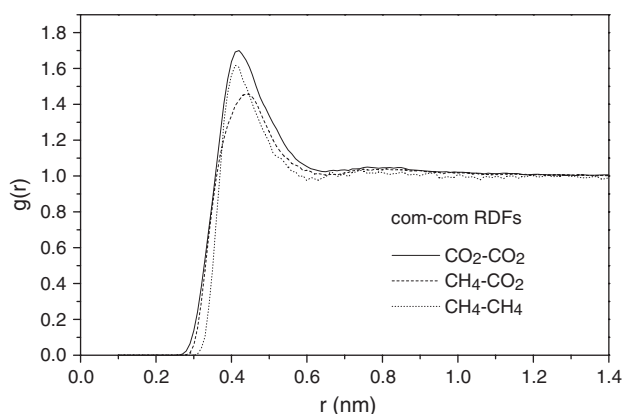


Fig. 1. Center of mass–Center of mass RPDFs.

Table 2

Positions and amplitudes for the first maximum and minimum in each com-RPDF from this study

com-com $g(r)$	I. First maximum position (nm): Amplitude	I. First minimum position (nm): Amplitude
CO ₂ -CO ₂	0.42:1.700	0.65:1.024
CH ₄ -CO ₂	0.44:1.458	0.65:1.005
CH ₄ -CH ₄	0.41:1.618	0.63:0.977

was based on the FCC lattice with density corresponding to the experimental one and then the molecules were randomly distributed in the simulation box in order to achieve a better mixing. The fluid was simulated for a time interval of 400 ps. From this period, the first 200 ps were regarded as the time interval to reach equilibrium and the rest to calculate the properties of the system.

3. Results and discussion

The most common thermodynamic properties of the system at the thermodynamic conditions under investigation, such as the average total energy, potential energy and pressure, mean square force and torque, have been evaluated and they are presented in Table 1. From the results in Table 1, we can easily see that the calculated pressure is in quite reasonable agreement with experiment [38]. As mentioned in the introduction, one of the main goals in this study has been the investigation of the intermolecular structure of the mixture in terms of the appropriate center of mass (com) and site-site RPDFs. In addition, based on these correlations it was possible to explore the local structure around the solute (CH₄) and solvent (CO₂) molecules by using the calculated local coordination numbers. It has been realized by integrating the corresponding RPDFs for the possible combinations, namely solvent-solvent, solute-solvent and solute-solute. The calculated com-com RPDFs are depicted in Fig. 1 and the positions and amplitudes up to the first maximum and minimum in each RPDF are summarized in Table 2.

By inspecting the behavior of these functions, we can clearly see that the position of the first minimum for both the solute-solvent and solvent-solvent RPDFs is located at 0.65 nm, whereas in the case of the solute-solute it is located at 0.63 nm. All the coordination numbers obtained are presented in Table 3. We can clearly observe that the coordination number of the solvent molecules around the solute is smaller than the corresponding number of the solvent molecules around the solvent.

Table 3

Coordination numbers around the solvent and solute molecules in the first coordination shell

Pair	Coordination number
CO ₂ -CO ₂	3.788
CH ₄ -CO ₂	3.527
CO ₂ -CH ₄	0.788
CH ₄ -CH ₄	0.775

In each molecular pair, the first molecule denotes the central one.

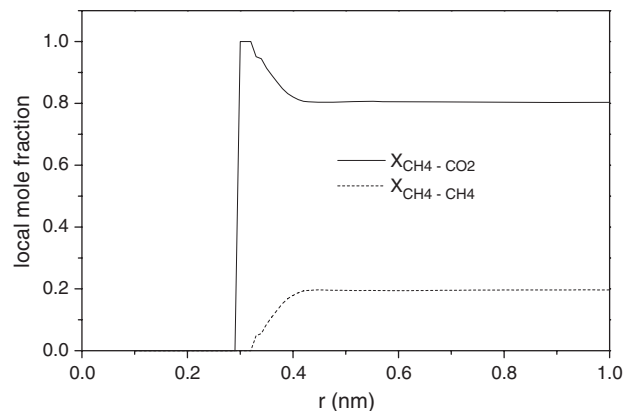


Fig. 2. Local mole fractions around methane.

By taking into account the fact that the corresponding coordination numbers are the average number of solvent molecules around the solute and solvent in their first coordination shells, respectively, we may conclude that the first solvation shell of methane consists of a smaller number of CO₂ molecules compared with the first solvation shell of CO₂. As also pointed out by Baglin et al. [37], and according to the results obtained from the present MD study the difference between the aforementioned coordination numbers ($n_{\text{solute-solvent}} - n_{\text{solvent-solvent}}$) was found to be negative. This fact indicates that the CO₂-CO₂ molecular interactions are stronger compared to the CO₂-CH₄ interactions in the mixture. Based on this conclusion the methane-carbon dioxide mixture might be characterized as a repulsive one. It should be mentioned here that this result is in agreement with the aforementioned previously reported experimental and theoretical results [37].

Concerning the solute-solute RPDF we may observe that the first non-zero value of this function is shifted to a larger distance in comparison with the solvent-solvent and solute-solvent RPDFs. This behavior indicates that the solute molecules are well segregated in the mixture.

Furthermore, in order to extract additional information on the local structure and composition around the solute and solvent molecules in the mixture, we have calculated the local mole fractions of both species around the solute and solvent

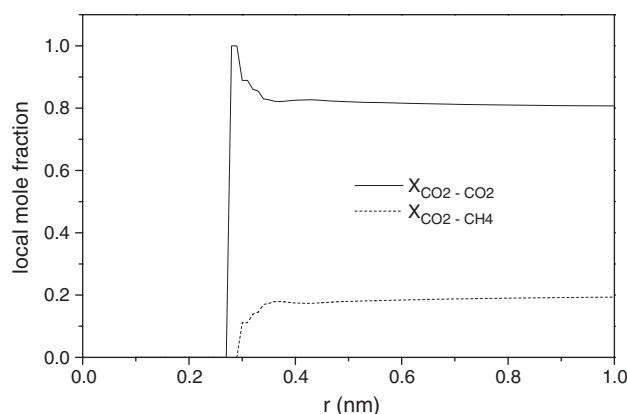


Fig. 3. Local mole fractions around carbon dioxide.

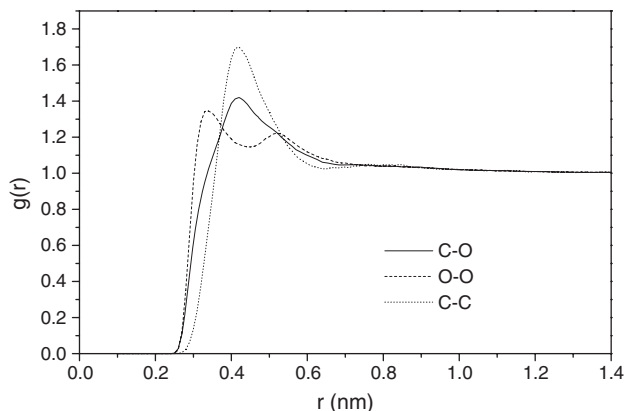


Fig. 4. Solvent-solvent site-site RPDFs.

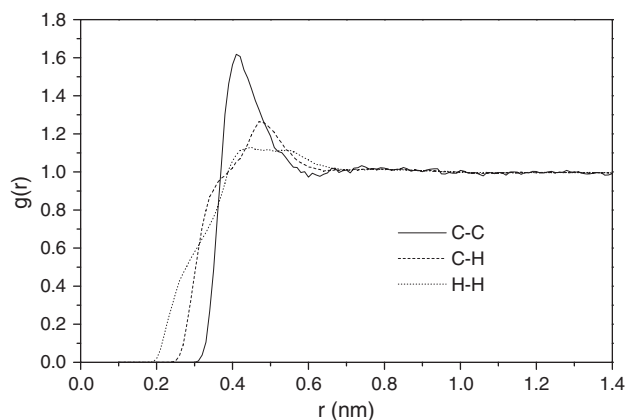


Fig. 6. Solute-solute site-site RPDFs.

molecules as a function of the distance from them, respectively, by using Eq. (1):

$$X_{i-j}(r) = \frac{n_{i-j}(r)}{n_{i-j}(r) + n_{i-i}(r)} \quad (1)$$

In Eq. (1), $n_{i-j}(r)$ denotes the corresponding local coordination numbers of the j molecules around a central i molecule (solute or solvent) which are evaluated from the following integral relation

$$n_{i-j}(r) = \rho_j \int_0^r 4\pi R^2 g_{i-j}(R) dR \quad (2)$$

where ρ_j is the number density of molecules j in the mixture.

The calculated local mole fractions around the solute (CH_4) and solvent (CO_2) molecules are depicted in Figs. 2 and 3, respectively. By inspecting these results we found that the local mole fraction of CO_2 and CH_4 around CH_4 decreases and increases, respectively, and this behavior is observed up to the distance point about 4 Å where they reach their bulk values. A similar behavior has been also predicted for the local mole fraction of CO_2 and CH_4 around CO_2 , which is somewhat different from those around CH_4 . Clearly, we can observe that the local mole fraction of CO_2 and that of CH_4 around CO_2 reach its bulk value at a distance of about 3.5 Å. Therefore, we can conclude that the deviation of the local mole fractions of the two components around CH_4 from their bulk values is

observed even at larger distances than in the case of the local mole fractions of the two components around CO_2 . However, we have to mention that at distances extended up to the radius of the first coordination shell the calculated local mole fractions in all cases have obtained their bulk values, as it is depicted from Figs. 2 and 3. This observation is clear evidence that no aggregation phenomena may be observed in the mixture [41]. This finding also supports the conclusions of Baglin et al [37], according to which “the methane moieties may be thought of as isolated islands between channels of carbon dioxide molecules”.

To obtain detailed information about the local structure around each molecule, we have also calculated the site-site RPDFs for the aforementioned molecule-molecule combinations. All these functions are depicted in Figs. 4–6.

We mainly focused on the behavior of the solute-solvent site-site RPDFs, since we are interested in the local structure around the solute. Regarding the H–O RPDF, we may observe that the main feature of this particular function is the existence of a characteristic small shoulder located at very short distances about 0.3 nm. Furthermore, we mention here that the first non-zero value of this function is located at a quite short distance of about 0.22 nm, something that is also observed in the H–C RPDF. The H–O RPDF exhibits a first peak with a rather low intensity of 1.214 at 0.45 nm, whereas

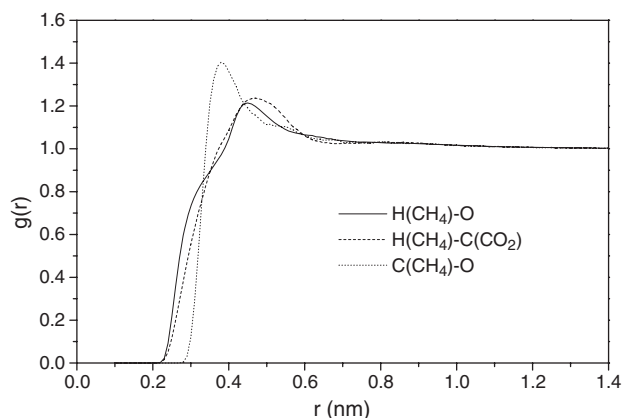
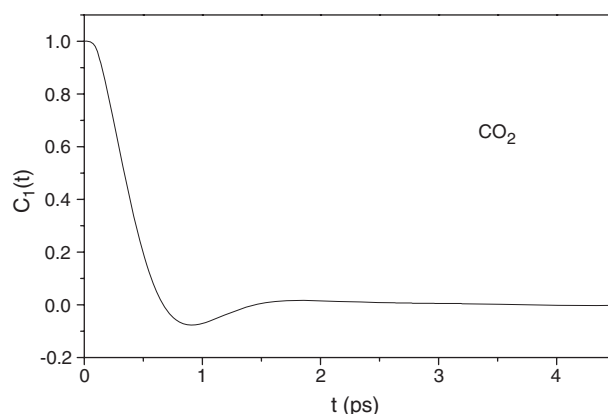
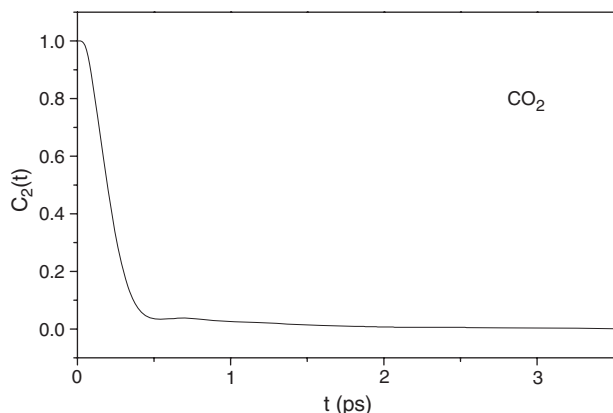


Fig. 5. Solute-solvent site-site RPDFs.

Fig. 7. Normalized first-order Legendre reorientational ACF for CO_2 .

Fig. 8. Normalized second-order Legendre reorientational ACF for CO₂.

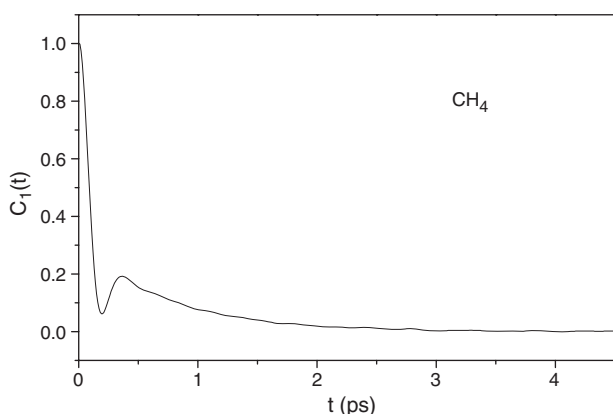
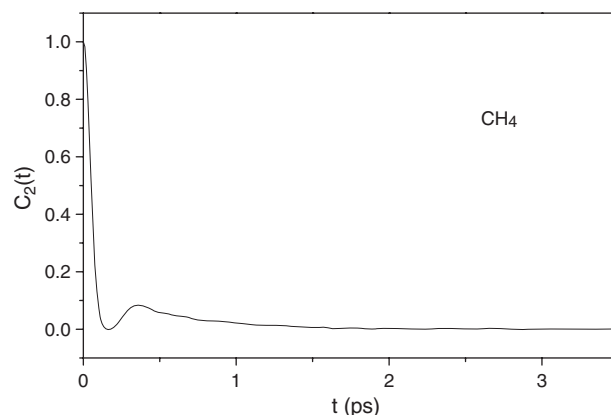
the H–C and C–O RPDFs exhibit a first peak with corresponding amplitudes 1.237 and 1.405 located at 0.47 and 0.38 nm, respectively. By inspecting the solute–solvent com-RPDF, which is the same with the C–C function, we can observe that the first peak is located at 0.44 nm with the corresponding amplitude of 1.458.

We have also investigated the single reorientational dynamics of the solute and solvent molecules by means of the first- and second-order Legendre autocorrelation functions (ACFs) of some specific unit vectors for each molecule. In the case of CO₂, we have used a unit vector along the C–O axis, whereas for the methane molecule, the unit vectors along the principal rotational axes of the molecule. Since the methane molecule is an isotropic one with tetrahedral symmetry T_d and the moments of inertia for each principal axis are the same, the corresponding ACFs for each unit vector along each rotational principal axis are identical. The Legendre reorientational ACFs have been calculated by using the well-known relation:

$$C_L(t) = \langle P_L(\vec{u}(0) \cdot \vec{u}(t)) \rangle, \quad L = 1, 2. \quad (3)$$

The corresponding Legendre reorientational ACFs for the solvent and solute molecules are depicted in Figs. 7–10.

The reorientational correlation times τ_1 and τ_2 for carbon dioxide and methane have been evaluated by integrating the corresponding normalized ACFs and are presented in Table 4.

Fig. 9. Normalized first-order Legendre reorientational ACF for CH₄.Fig. 10. Normalized second-order Legendre reorientational ACF for CH₄.

By inspecting carefully these ACFs, we observe a quite interesting time dependent behavior regarding the reorientational dynamics of the methane molecules. Both the first- and second-order Legendre reorientational ACFs of methane decay very rapidly during the period 0–0.2 ps. At $t=0.2$ ps, these functions exhibit a local positive minimum. In the time interval 0.2–0.37 ps the ACFs increase and they exhibit a local maximum at $t=0.37$ ps. After this period, the ACFs decay very smoothly until they reach their zero values at about 3.5 ps. We may therefore conclude that during a very small time period the reorientational motion of the methane molecules in their molecular cages lose its correlation very rapidly and then recovers correlation until $t=0.37$ ps, when the correlation starts again to decay in a more smooth way until it becomes zero.

Concerning the behavior of the corresponding ACFs for carbon dioxide we may conclude that its reorientational dynamic behavior is not very much affected from the presence of the solute molecules. According to the nuclear magnetic resonance (NMR) measurements of pure SC CO₂ by Umecky et al. [42] at a slightly higher temperature of 331.8 K and about the same density with the simulated mixture in this study, the reorientational correlation time, τ_2 , has been found to be 0.270 ps. Furthermore, Holz et al. [43] in their NMR experimental measurements of pure SC CO₂ at $T=319$ K, have also reported a value of $\tau_2=0.21$ ps for CO₂ at a similar density with that previously mentioned. In our simulation studies, we have calculated a value of 0.252 ps for CO₂, which comes in reasonable agreement with experiment. Moreover, by inspecting the Legendre reorientational ACFs of CO₂, we may suggest that the shape of these functions comes in agreement with the results obtained from a previous simulation of pure SC–CO₂ at $T=307$ K and at a similar density [44]. Although the behavior of $C_1(t)$ of CO₂ in the mixture is not different from the corresponding one in pure CO₂ at the same density, this does

Table 4
Reorientational correlation times τ_1 and τ_2 for carbon dioxide and methane from this study

	τ_1 (ps)	τ_2 (ps)
CO ₂	0.332	0.252
CH ₄	0.256	0.103

not mean that the rotational dynamics of CO₂ in the mixture exhibit an overall gas-like behavior. In our case, the reorientational correlation times are found to be very small. This is an indication that the rotational dynamics of the CO₂ molecules in the mixture exhibit similarities with gas-like behavior. However, the non-zero value of the reorientation correlation times leads us to assume that the influence of molecular collisions in the determination of the shape of these correlations is not negligible.

4. Concluding remarks

In the present MD treatment, we have studied the behavior of the binary SC mixture methane–carbon dioxide at $T=323.15$ K. In this study, methane has been used as the solute in the mixture with mole fraction $X=0.2$, and carbon dioxide as the solvent. From the results of the present simulation, it was possible to investigate the repulsive or attractive behavior between the solute and solvent molecules and to gain further insights into the solvation process for this binary SC fluid. It has been examined in terms of the calculated appropriate RPDFs, which have been used for the prediction of the local coordination numbers and local mole fractions around the species in the mixture. The main conclusion, which can be drawn from the present study, is that the system methane–carbon dioxide at SC conditions might be identified as a repulsive one, a result that is in accordance with previous interaction induced Raman light scattering investigations of the same mixture at comparable concentrations [37]. We have also investigated the single reorientational dynamics of the solute and solvent molecules in the mixture and the results obtained have been discussed and compared with previous experimental and simulation studies.

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