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Abstract

Neutron and x-ray diffraction results obtained for liquid CO_2 have been modelled by means of the reverse Monte Carlo method. Partial pair correlation functions, centre–centre pair correlation functions and relative orientations of molecular axes as a function of distances between molecular centres have been calculated from the models. It was found that well defined orientational correlations exist in the liquid state. Close to the critical point, these correlations seem to disappear, but further away from the critical point, in the high density supercritical state, they reappear. Using large particle configurations, the density fluctuations close to the critical point could be visualized.

1. Introduction

Carbon dioxide is one of the best known and most important materials in our lives—for example let us just mention its role in the process of photosynthesis among many other things (for a quick source of information, see [1]). The liquid/fluid phase of carbon dioxide is also significant: it is being used in growing volumes as a special and, in many cases, specific solvent for organic materials [2]. Industrial applications of (supercritical) fluid carbon dioxide are made feasible by the accessibility of the supercritical regime: the critical point is at 304.1 K and 73.8 bar which corresponds to a molecular number density, $\varrho_M = 0.0064$ Å^{-3}; a typical density value for the liquid is $\varrho_M = 0.0161$ Å^{-3}, measured at the triple point (216.6 K, 5.2 bar).

Detailed understanding of the microscopic structure of liquid/supercritical fluid CO_2 may help to understand the mechanism of solvation. This was recognized a while ago [3], and as a result a wealth of diffraction measurements, over wide ranges of temperature and pressure, have been carried out with the aim of providing a microscopic picture of the structure [4–14]. Most of these works aimed at determining the pair correlation function (PCF), although some of them attempted to provide a qualitative description of the local orientations too. For instance, Ishii [12] suggested that in the supercritical state at higher densities 'T-shaped' and 'cross-shaped' arrangements are characteristic (for a more precise definition of our correlation

functions, see below), whereas at lower densities 'T-shaped' and 'shifted parallel' arrangements are the characteristic ones. The importance of the 'T-shaped' arrangement is emphasized in several publications [11, 13, 14].

Molecular dynamics (MD) simulation studies also abound; the latest ones [15, 16] show respectable agreement with diffraction data. As far as orientational correlations are concerned, the 'T-shaped' arrangement was found to be the most important, and became more and more distorted as density decreased.

Bertagnolli [17] applied a reverse Monte Carlo like procedure (see below) for describing the intermolecular pair correlation functions obtained by Bausenwein [6] for supercritical states well above the critical point. They found that at the highest densities parallel arrangements were the most likely to occur whereas at lower densities the probability of finding T-shaped and parallel configurations was the same. This study excluded the occurrence of cross-shaped arrangements.

Despite the vast literature on the structure of liquid CO_2, a comprehensive structural study covering the gaseous, liquid and supercritical fluid phases of the material seems to be lacking. The primary aim of the present investigation is to look at the microscopic structure of the above phases of carbon dioxide by constructing large structural models that are consistent, to within experimental errors, with available diffraction data. Reverse Monte Carlo (RMC) modelling [18, 19] was applied to generate the models (particle configurations). Based on the atomic coordinates, specific mutual molecular arrangements, like 'T-shaped', 'parallel', 'chain-like', etc, were searched for, in order to be able to describe orientational correlations using the same terms as already found in the literature [12–14, 16, 17].

It may be noted that we have already studied the structure of liquid carbon monoxide, CO, using the same 'protocol' (RMC modelling of diffraction data, followed by an extensive search for special arrangements of neighbouring particles) [20] and a similar project on homonuclear diatomic molecular liquids has also been completed [21]. The structure of carbon dioxide appears to be of intermediate complexity between fluids of homonuclear diatomic molecules (such as N_2) and of molecules with a real three-dimensional shape (such as CCl_4). That is, liquid CO_2 fits well into the series of systematic studies on simple molecular liquids that has been carried out in our laboratory [22–25].

2. Reverse Monte Carlo calculations

Details of the reverse Monte Carlo method can be found in several publications [18, 19, 26, 27], so that only specifications for the current calculations are given here.

In each case, 5000 molecules (15 000 atoms) were put in cubic boxes. In each simulation, several hundred successful moves/atom were completed. Molecules were flexible, which was made possible by the application of 'fixed neighbour constraints' (fnc) [27, 28]. The intramolecular C–O bond was allowed to vary between 1.11 and 1.21 Å. Calculations were conducted using the *rmc_fi* software [28], with a modification necessitated by the rather strict linearity of the CO_2 molecule: the intramolecular O–C–O angles were kept between 170° and 180°. Such a construction kept the intramolecular O–O distance around its equilibrium value of 2.3 Å, so that additional (separate) constraining of this distance was not necessary.

Some details of the successful RMC calculations are given in table 1. Figure 1 shows a schematic phase diagram for carbon dioxide [29], where successful RMC calculations are denoted by markers. It is obvious that quite a large region of the $T–p$ plane could be mapped in the present work, which forms the basis of a comprehensive structural study.

Hard sphere Monte Carlo calculations of molecular systems, with the same parameters (density, bond-length constraints, cut-offs etc) as the RMC runs, have also been carried out for

Table 1. Diffraction experiments on liquid, supercritical fluid and gaseous carbon dioxide. 'N' and 'X' denote neutron and x-ray diffraction, respectively; ϱ_M is the molecular density. 'L', 'SC' and 'G' stand for liquid, supercritical and gaseous states, respectively.

Reference	Experiment	T (K)	p (bar)	State	$\varrho_M \left(\frac{\text{molecules}}{\text{Å}^3} \right)$	RMC successful
[4]	N	222	6.5	L	0.0158	Yes
		239	14.5		0.0149	
		220	58	L	0.0161	Yes
[5]	N	290	60		0.0112	
		303	77	L	0.0093	
			60	G	0.0024	Yes
			227		0.00684	
[6]	N	380	361	SC	0.00958	
			741		0.01232	
[7]	N	220	8.5	L	0.01597	Yes
		313.3	91.4	SC	0.00700	
[8]	X	306.7	81.5		0.00846	
		277.4	68.2	L	0.01262	
			92		0.00460	
[9]	N	320	97	SC	0.00542	Yes
			102		0.00645	Yes
[10]	N	310	101	SC	0.00952	Yes
[11]	N	313	660	SC	0.0140	Yes
			86		0.00748	Yes
[12]	N	311	81	SC	0.00488	
			61		0.00218	
		277.6	68.2	L	0.0126	
			93.4		0.00934	
[13]	X		91.2		0.00916	
		308.2	84.0	SC	0.00809	
			81.2		0.00671	
			76.7		0.00427	
[14]	N	239	16	L	0.0149	Yes

each state. The easiest way to do this is by running the RMC without fitting experimental data. These calculations provided reference structures which possess all features that originate from excluded volume (pure steric) effects. Differences between hard sphere and RMC structures are characteristic of the nature of intermolecular interactions. This rather simple way of interpreting diffraction results and corresponding RMC models has proved remarkably useful in the past [22].

There are different methods for the characterization of mutual orientations of molecules [20, 30, 31]. Here, distance dependent orientational correlation functions were calculated in the following admittedly *ad hoc* manner [20]: angles confined by the molecular axes and the line connecting molecular centres were calculated. For any given pair of molecules, two such angles exist. With the help of an additional angle, confined by the two molecular axes, any given popular mutual orientation of two molecules, like 'parallel', 'T-shaped', 'chain-like', etc can be characterized. Allowing a rather wide spread for the cosines of these three angles, ±0.25, the number of pairs that realize one of the well-known configuration
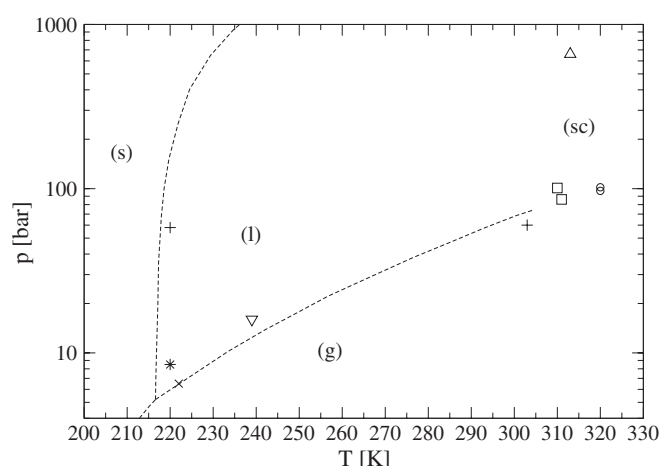
Figure 1. Reverse Monte Carlo studies reported in the present contribution, as placed on a schematic phase diagram of carbon dioxide: ×, from [4]; +, from [5]; ∗, from [7]; O, from [9]; △, from [11]; □, from [12]; ▽, from [14].

has been calculated as a function of the distance between molecular centres. The number of these counts was then divided by the total number of pairs (independent of the orientation) that could be found in the same distance-bin. (That is, the normalizing factor was the centre–centre pair correlation function.) Finally, the asymptotic value (at $r = \infty$) was rescaled so that for each particular orientation the asymptotic value would be unity. These correlation functions can be interpreted in a similar way to what is customary for pair correlation functions—the essential difference being that the connection to absolute quantities is lost. For this reason it is important to report (or at least, to give an indication of) the number of pairs realizing a given mutual orientation at a given distance. Throughout this study, the smallest distance where at least a few tens of pairs (in a given single particle configuration, for the given specific arrangement) could be found will be given, so that statistics would be reasonable. These distances are denoted by vertical bars in the corresponding figures (see below). In this work, depending on the exact thermodynamic state, orientational correlations have been calculated over at least 17 independent configurations, separated by an average of 360 000 accepted moves.

3. Results and discussion

Figure 2 compares the 10 experimental structure factors to the $F(Q)$s of the corresponding RMC models. Reproduction of experimental data may be termed perfect in each case; it is fair to remind the reader, however, that this does not guarantee that the structural models are meaningful. The good agreement between model and experiment is particularly noteworthy in the near-critical cases, around 310 K: it seems that the simulation boxes were big enough to contain density fluctuations that cause the large small angle scattering signal.

C–C partial pair correlation functions, as calculated directly from particle configurations, are shown in figure 3. Note that these partials are the molecular centre–molecular centre (mc–mc) correlation functions too. The figure contains the mc–mc correlation functions for the corresponding hard sphere reference systems as well. In the region of liquid-like densities, the reference functions provide fairly close comparisons to results of RMC modelling. On the other hand, at lower densities, in the supercritical and gaseous (see figure 4) states, the position
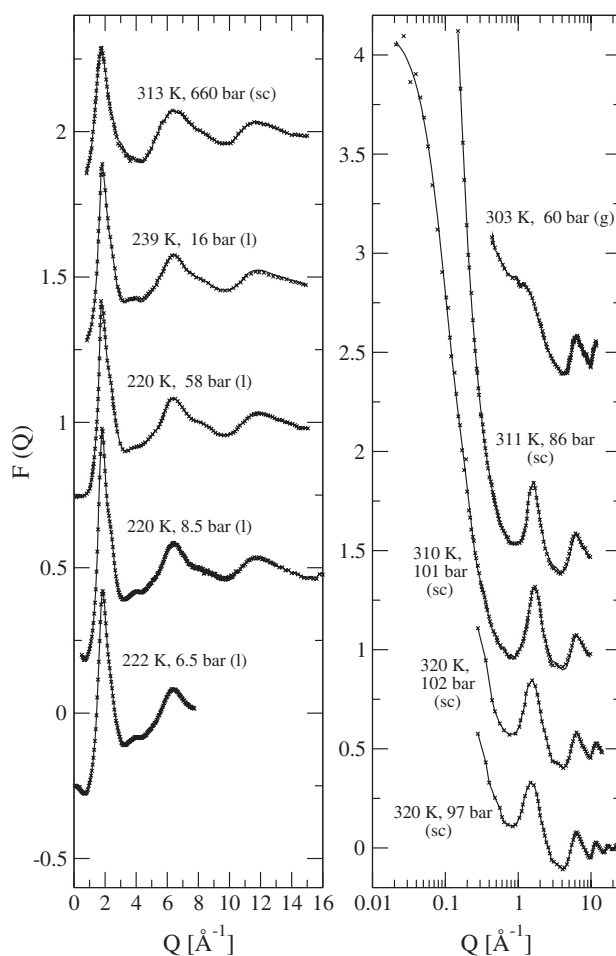
Figure 2. Experimental (symbols) and RMC simulated (solid line) structure factors for condensed phases of carbon dioxide. 'l' denotes state points in the liquid phase, whereas 'sc' and 'g' refer to the supercritical and gaseous phases, respectively.

of the first peak is shifted towards lower r-values in the 'real' (RMC simulated) systems. This phenomenon may be explained by the presence of attractive forces acting between molecules: these forces bring molecules closer together than would be expected on the basis of the average number density. In the gaseous state (figure 4) this causes the first maximum of the mc–mc (identical to the C–C partial) pair correlation function to nearly disappear. That is, at the C–C PCF level, the real system appears to be more disordered than the corresponding reference system. In the near critical states, the consequence is the formation of (correlated) density fluctuations.

The O–O and C–O partial PCFs (not shown) behave as expected, possessing large intramolecular maxima followed by only one well recognizable intermolecular peak. This latter for the C–O case seems to show a weak tendency to split at higher pressures in the normal liquid region.

We now turn to our main subject, the description of orientational correlations found in the different phases of carbon dioxide. First, let us consider the 'normal' liquid states, close to
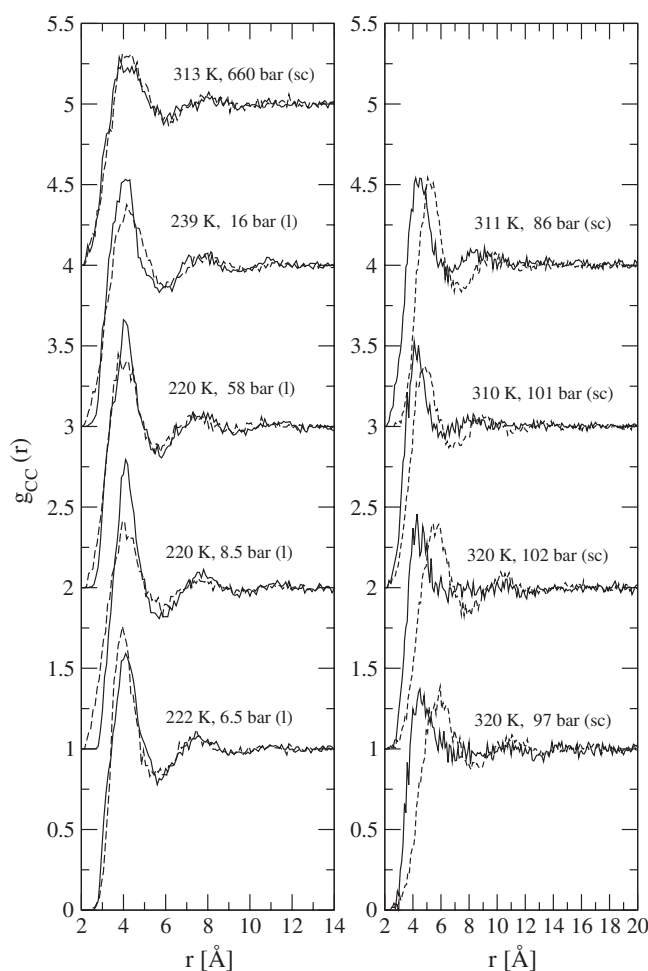
Figure 3. C–C partial pair correlation functions of CO_2 in the liquid and supercritical fluid phases, as obtained directly from particle coordinates. Solid line, RMC models; dashed line, reference (hard sphere) systems. Note that this partial is, at the same time, the molecular centre–molecular centre pair correlation function.

the triple point of the material. Figure 5 displays results for the four state points considered in this region, with temperatures ranging between 220 and 239 K and pressures between 6.5 and 58 bar. The most striking features are undoubtedly the very strong peaks of the orientational correlation functions representing the parallel and the cross-shaped arrangements at the closest distances, around 3 Å. A significant occurrence of the 'T-shaped' arrangement can be found at higher centre–centre (C–C) distances, at around (or a little above) 4 Å—this is the region of the first maximum of the centre–centre pair correlation function. Finally, a little above 5 Å, which is the region of the first minimum of the centre–centre PCF, chain-like arrangements become somewhat more abundant than they are in the corresponding reference system. Each 'specific' correlation function differs significantly from the corresponding reference function, indicating a higher level of ordering in the 'real' system. As these states are among the ones with the highest density, it is evident that the present results may be in contradiction with earlier experimental findings [12–14] where the dominance of the T-shaped arrangement was suggested at higher,
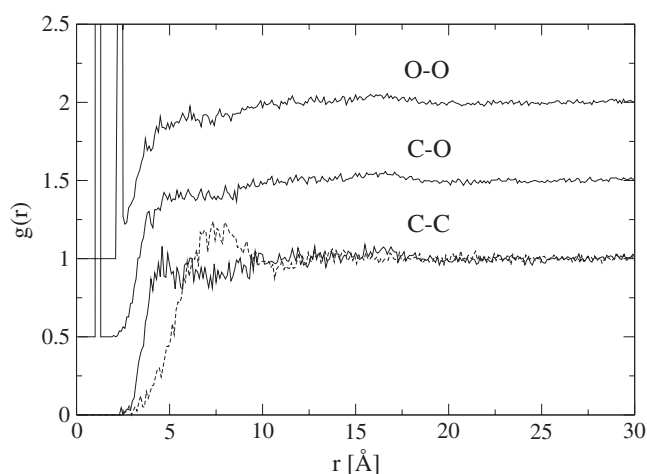
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Figure 4. Partial pair correlation functions of CO_2 in the gas phase, as obtained directly from particle coordinates. Solid line, RMC models; dashed line, reference (hard sphere) systems (for the C–C partial only). The curves are shifted along the y-axis for clarity by 0.5.

liquid like, densities in the supercritical state (although the cross-shaped and 'shifted parallel' configurations are, at least, mentioned). It may be noticed that our results are based on large structural models that are in full consistency (quantitative agreement) with experimental data; from the experimental studies mentioned the modelling stage was missing. Recent molecular dynamics simulation studies [15, 16] discuss the T-shaped arrangement exclusively at high densities; their interatomic potential models seem to have missed the other (competing) arrangements. The present results resemble those of Bertagnolli [17], although the temperature and pressure there were much higher than considered here. Note that our discussions above hold for all experiments in this group of state points, even though the structure factors are from different measurements, performed by different groups on different instruments. The high level of consistency between these sets lends further support to the present findings.

Figure 6 displays similar specific orientational correlation functions for a high density supercritical state (313 K, 660 bar). At the shortest significant distances, about 3 Å, the dominance of the parallel arrangement is evident (even though the ratio of such a recognizable arrangements is smaller than it was in the liquid phase close to the triple point). In this respect, the high density supercritical state is similar to the normal liquid, a similarity which would be expected if the local ordering were purely density driven (a similar density gives similar local orientations, with negligible influence of the actual (p, T) values). However, important differences are also apparent: the cross-shaped arrangements seemed to have lost their significance (especially because the number of recognizable pairs decreased strongly) and the T-shaped pairs have disappeared entirely from the region of the first maximum of the centre–centre PCF. As a general remark, here the reference functions nearly match the 'real' ones resulting from fitting data, indicating that at high p and T (well above the critical point), excluded volume effects are mainly responsible for any recognizable local ordering. This picture is in qualitative agreement with that of Bertagnolli [17].

In figure 7 specific orientational correlation functions for four states in the supercritical region, near the critical point, are introduced. Even though the state points are rather close to each other, clear tendencies are revealed by the local orientations as a function of the distance from the critical point. Closest to it (311 K, 86 bar) the abundance of parallel arrangements is
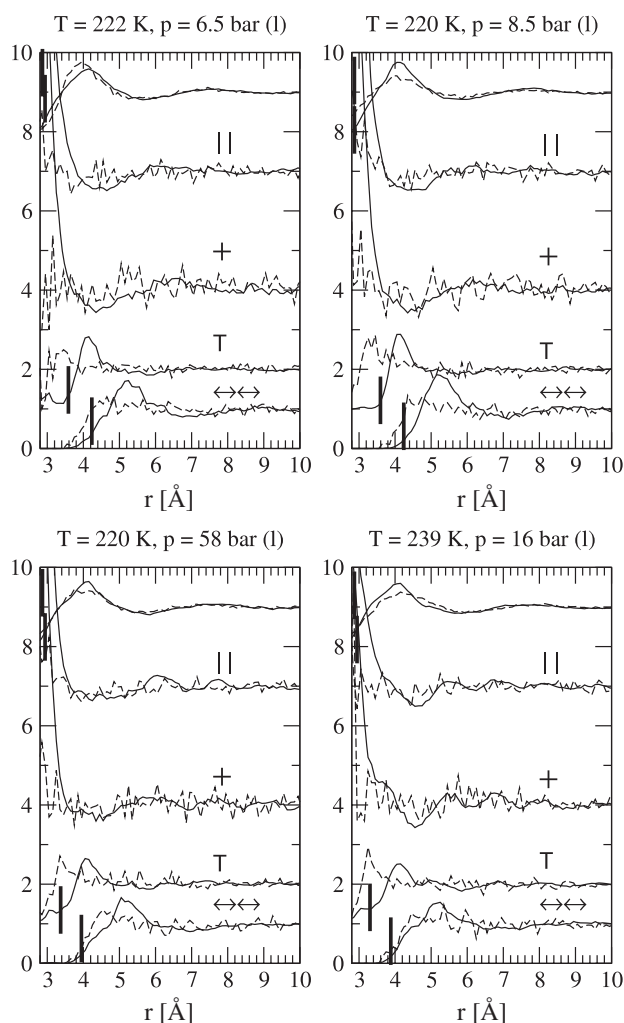
Figure 5. Orientational correlation functions for liquid CO_2. Solid lines, RMC models; dashed lines, hard sphere reference systems. The pictograms denote (starting with the lowermost curve in each panel) chain-like, T-shaped, cross-shaped and parallel arrangements. The centre–centre correlation functions are also shown for comparison (uppermost curves). Vertical bars show the 'significance limits', above which distance the number of pairs of molecules was sufficient for achieving decent statistics for the given arrangement. (The curve pairs are shifted along the y-axis for clarity.)

about as low as that of the T-shaped configurations. Note that this is the only state where the T-shaped arrangements previously thought to be dominant are equally characteristic as the parallel ones. Here, the level of correlations in general is extremely low: the functions exhibit only very slightly higher ordering than found in the reference systems. Increasing the pressure somewhat (310 K, 101 bar) immediately results in a noticeable increase in terms of the occurrence of parallel shaped pairs, while the number of T-shaped pairs remains unchanged. Increasing the temperature by only 10 K (320 K, 97 bar and 322 K, 102 bar) brings about a significant increase in the number of parallel mutual configurations which nearly reaches the level found at a much higher density (see above, 313 K, 660 bar). It seems obvious that fluid carbon dioxide displays
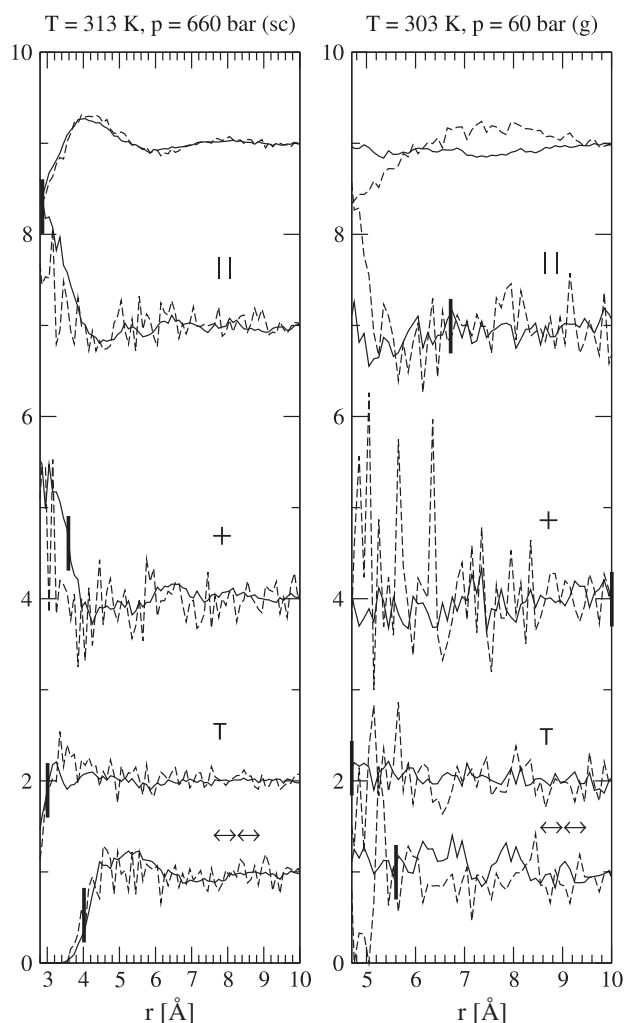
Figure 6. Orientational correlation functions for high density supercritical (left panel) and gaseous (right panel) CO_2. Solid lines, RMC models; dashed lines, hard sphere reference systems. The pictograms denote (starting with the lowermost curve in each panel) chain-like, T-shaped, cross-shaped and parallel arrangements. The centre–centre correlation functions are also shown for comparison (uppermost curves). Vertical bars show the 'significance limits', above which distance the number of pairs of molecules was sufficient to achieve decent statistics for the given arrangement. (The curve pairs are shifted along the y-axis for clarity.)

an unexpectedly rich 'orientational phase diagram', with a well defined 'focal point', the critical point. In other words, the location of the genuine critical point could be found on the pure basis of specific orientational correlation functions, or indeed just by monitoring the abundance of parallel mutual arrangements (see below).

In reference to most of the earlier suggestions based on experimental [12–14] and MD simulation [15, 16] evidence concerning the supercritical fluid region of the phase diagram of carbon dioxide it is clear that the present results are significantly different. We see no reason why any discussion of the local orientations should be based on the occurrence of the T-shaped arrangements, since this type of arrangement has hardly any importance. Instead,
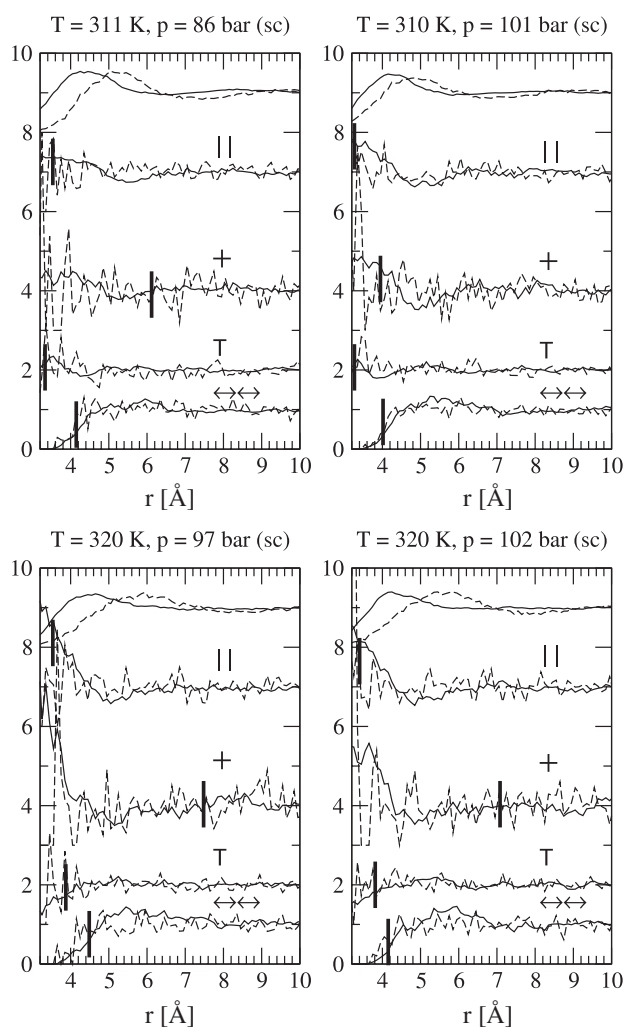
Figure 7. Orientational correlation functions for supercritical fluid CO_2, near the critical point. Solid lines, RMC models; dashed lines, hard sphere reference systems. The pictograms denote (starting with the lowermost curve in each panel) chain-like, T-shaped, cross-shaped and parallel arrangements. The centre–centre correlation functions are also shown for comparison (uppermost curves). Vertical bars show the 'significance limits', above which distance the number of pairs of molecules was sufficient to achieve decent statistics for the given arrangement. (The curve pairs are shifted along the y-axis for clarity.)

parallel arrangements are more abundant; indeed, over the entire (sub- and supercritical) fluid region, they may be used as indicators of the level of local orientational correlations.

We note that figure 6 contains specific orientational correlation functions for the gaseous state too. As might be expected, no recognizable correlations were found.

Finally, the issue of density fluctuations in the near-critical and supercritical states is addressed briefly. Based on the structure factors (see figure 2), as well as on common sense, large density fluctuations are expected close to the critical point which mostly disappear at much higher pressures in the supercritical region. Figure 8 shows projections of atomic density maps for three states: one is a liquid close to the triple point, the next one is close to and the
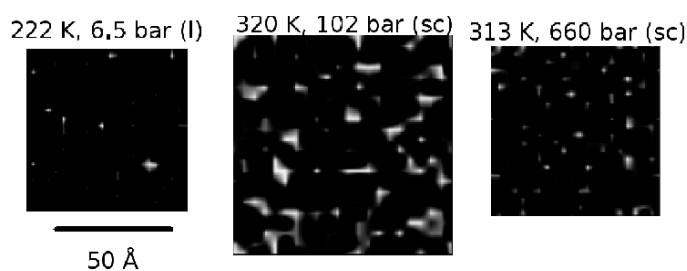
Figure 8. Two-dimensional projections of atomic density maps for normal liquid (left), near-critical supercritical fluid (middle) and high density supercritical fluid (right) CO_2. The pictures were taken on 3–4 Å thick layers (depending on the edge length of the simulation cell), containing roughly 240 molecules.

third one is far from the critical point. In agreement with common-sense expectations, there are large fluctuations visible in the particle configuration corresponding to a thermodynamic state close to the critical point, whereas far from the critical point in the supercritical region the fluctuations are much less visible. The normal liquid shows an even distribution of the local density (within errors).

4. Conclusions

Based on large structural models that are fully consistent with experimental structure factors of liquid carbon dioxide over a wide region of the phase diagram it could be established that well defined orientational correlations exist in the material, particularly in the 'normal' liquid state (close to the triple point) and in the high density supercritical state. In contrast to most of the previous suggestions, the dominant mutual arrangement of CO_2 molecules appears to be the parallel one; T-shaped local configurations are much less important.

Considering the importance of the material, particularly in the supercritical region, further experiments can be envisaged. There is an appreciable contrast between neutron and x-ray diffraction, so that by using structural modelling simultaneously on the two data sets the separation of the partial pair correlation functions, and consequently the determination of orientational correlation functions, could be made more precise.

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