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Orientalional correlations in liquid carbon monoxide and nitric oxide

L Temleitner and L Pusztai

Research Institute for Solid State Physics and Optics, PO Box 49, H-1525 Budapest, Hungary

E-mail: temla@szfki.hu

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Abstract

Neutron diffraction results obtained for liquid CO and NO have been modelled by means of the reverse Monte Carlo method. Partial pair correlation functions, centre–centre pair correlation functions and the relative orientations of molecular axes as a function of distances between molecular centres have been calculated from the models. It was found that, contrary to earlier suggestions, well defined orientational correlations exist in liquid carbon monoxide, even at lower densities. For liquid nitric oxide, the existence of (NO)₂ dimers has been confirmed, but the ‘cis-planar’ structure of the dimers, suggested earlier, could not be made consistent with available diffraction data.

1. Introduction

CO and NO are the simplest and probably the best known heteronuclear diatomic molecules. Their liquid phases, which are relatively easily accessible, provide the simplest examples where partial pair correlation functions may be applied for the description of the microscopic structure of a molecular liquid. In other words, the structure of carbon monoxide and nitric oxide appear to be of intermediate complexity between fluids of homonuclear diatomic molecules (such as N₂) and of molecules with a real three dimensional shape (such as CCl₄). Therefore, liquid CO and NO fit perfectly into the systematic studies of simple molecular liquids that is being carried out in our laboratory (see, for example, [1–3]).

The most recent experimental studies of the structure of liquid CO are those of Howe *et al* [4] and Bellisent *et al* [5]. Following fairly detailed inspection (including computer simulation) of their results, both studies conclude that orientational correlations cannot be found in the liquid at the densities they considered. (We note that a molecular dynamics study on liquid CO at higher densities [6] did find strong orientational correlations—but it failed to reproduce measured diffraction data.)

Howe *et al* [4] also report neutron diffraction measurements on liquid NO (which, to our best knowledge, is the only source of diffraction results on this liquid). They applied isotopic substitution on the nitrogen, using both ^{14}N and ^{15}N isotopes, and obtained two experimental total structure factors (tsfs), $F(Q)$. Based on a simultaneous analysis of the two tsfs, Howe *et al* [4] found their data consistent with a high degree (about 90%) of dimerization of NO molecules. They also suggest that the ‘cis-planar’ model of the $(\text{NO})_2$ dimer, that had been described earlier for the crystalline phase by x-ray diffraction [7, 8], is applicable for the liquid phase, as well. (Note that [15] of [4] refers to a Raman scattering study [9] and *not* an x-ray diffraction one, as mentioned.) Further details of the orientational correlations are not discussed in [4].

The primary aim of the present investigation is to look at the microscopic structure of liquid CO and NO by constructing large structural models of the liquids that are consistent (to within experimental errors) with available diffraction data [4, 5]. Reverse Monte Carlo (RMC) modelling [10] will be applied for the generation of models (particle configurations). Based on the atomic coordinates, specific mutual molecular arrangements (like ‘parallel’, ‘chain-like’, etc. . .) are searched for, in order to be able to describe orientational correlations.

2. Reverse Monte Carlo calculations

Details of the reverse Monte Carlo method can be found in several publications (see, for example, [10–12]), so that only specifications for the current calculations are given here.

For both liquid CO and NO, 5000 molecules (10 000 atoms) were put in cubic boxes. In each simulation, a minimum of 600 successful moves were completed per atom.

Liquid CO was studied at the two thermodynamic states described in [5]. The denser system was at a temperature $T = 83.5$ K and a pressure $P = 4.1$ bar, with an atomic number density of $\rho = 0.0342 \text{ \AA}^{-3}$; the corresponding boxlength was $L = 66.1 \text{ \AA}$. For the other, near-critical, state the temperature was $T = 121.9$ K and the pressure was $P = 23.0$ bar, which resulted in an atomic density of $\rho = 0.0240 \text{ \AA}^{-3}$ and a boxlength of $L = 74.6 \text{ \AA}$. The CO data of Howe *et al* [4] were also considered; these data had been taken at 120 K and 19 bar, with $\rho = 0.02463 \text{ \AA}^{-3}$ and $L = 74.0 \text{ \AA}$, which is practically the same as the near-critical state of Bellisent *et al* [5]. The intramolecular C–O distance was allowed to vary within the range of 1.09–1.19 Å by ‘fixed neighbours constraints’ [12, 13] for each calculation. Figure 1 compares the three experimental structure factors to the $F(Q)$ s of the corresponding RMC models.

Liquid NO was studied at $T = 120$ K and $P = 1.1$ bar, under which conditions the atomic number density was $\rho = 0.0509 \text{ \AA}^{-3}$; the length of the simulation box was then 58.0 Å. The intramolecular N–O distance was kept between 1.11 and 1.21 Å. Nitric oxide at this temperature and pressure is known to form dimers [14]. In order to check whether a high proportion, of the order of 90%, of dimers is consistent with diffraction results, a coordination constraint for the intermolecular N ··· N distance was introduced. This constraint required that 90% of the N atoms in the simulation box have exactly one N neighbour between 2.2 and 2.6 Å. This requirement could be fulfilled easily. On the other hand, further constraining the shape of the dimer and enforcing the ‘cis-planar’ arrangement [7, 8] was not possible.

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 each material. (The easiest way for this is running RMC without fitting experimental data.) These calculations provided reference structures, which possess all features that can be assigned to excluded volume (pure steric) effects. Differences between hard sphere and RMC structures are characteristic to the nature of intermolecular interactions. This—rather simple—

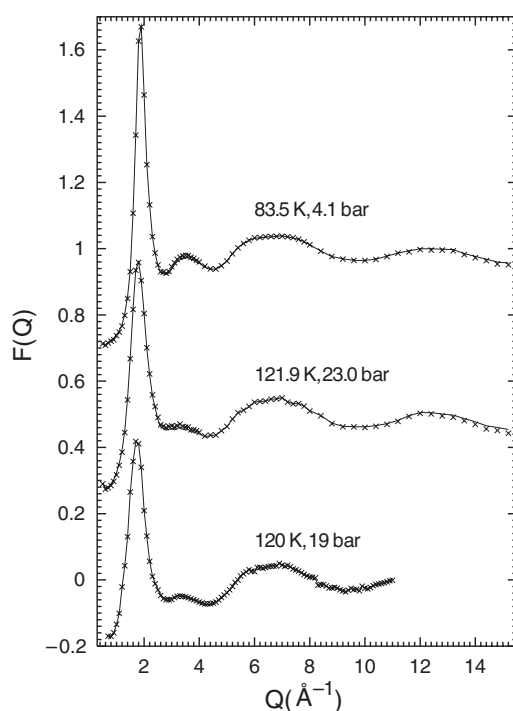


Figure 1. Experimental ([4] and [5]—see text for details) (symbols) and RMC fitted (solid curve) structure factors of liquid carbon monoxide. (The curve pairs are shifted along the y-axis by 0, 0.5 and 1.0, respectively.)

way of interpreting diffraction results and corresponding RMC models proved remarkably useful previously [1].

Distance dependent orientational correlation functions were calculated by the following—admittedly, ad hoc—manner: angles confined by the molecular axes and the line connecting molecular centres have been 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’, or ‘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 has been calculated as a function of the distance between molecular centres. The number of these counts has then been 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 could be found (so that the statistics would be reasonable) will be given. In this work, orientational correlations have been calculated over six independent configurations (separated by an average of 200 000 accepted moves) for each RMC run.

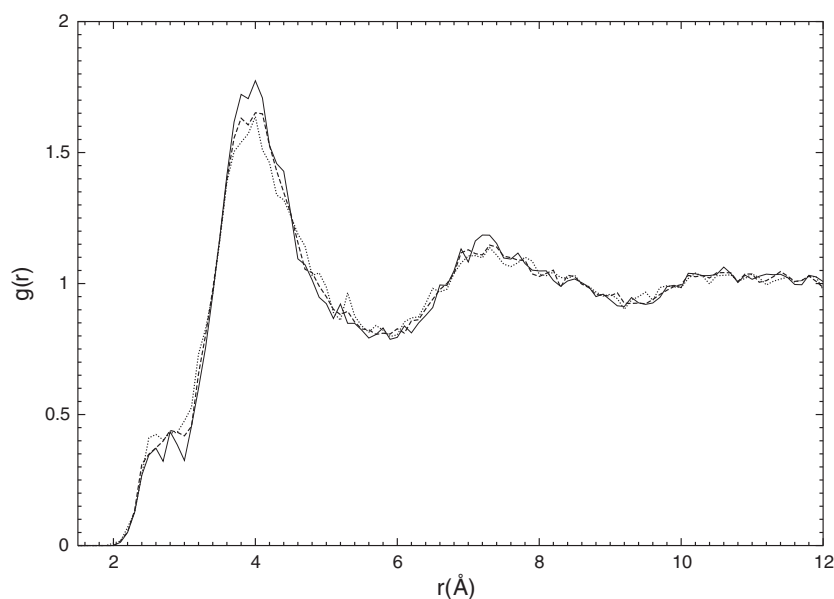


Figure 2. Partial pair correlation functions of liquid CO at 83.5 K, as calculated from the corresponding RMC model. Solid curve: C–C; dashed curve: C–O; dotted curve: O–O.

3. Results and discussion

3.1. Liquid carbon monoxide

Figure 1 compares the three experimental structure factors to the $F(Q)$ s of the corresponding RMC models. Reproduction of experimental data may be termed perfect; note, however, that this does not guarantee that the structural models are meaningful. (Quantitative agreement between RMC models and experiment is only a necessary, but not sufficient, condition for a physically meaningful description of the microscopic structure.)

Partial pair correlation functions for the denser state (at 83.5 K) of CO, as calculated directly from particle positions, are shown in figure 2. The first thing to notice is that there are no significant differences between the partials, which indicates that the reproduction of the single total structure does not necessitate, even at this higher density, further distinction. Neutron weights for the C–C, C–O and O–O partials are 0.11, 0.19 and 0.08, respectively. The x-ray weighted total structure factor would have somewhat different partial contributions, the O–O partial being represented there the most strongly; thus, if confirmation of the uniform ppcfs is needed, one may turn to x-ray diffraction. However, it seems unlikely that the strong differences between partials found by molecular dynamics simulations [6] are real. Another point to note is that the small, but distinct, shoulder on the low- r side of the first maxima could not be made to disappear, so that it may be considered as a real feature. Bellisent *et al* [5] did not report this shoulder; on the other hand, they show a rather slow onset of their $g(r)$ around the same region.

C–C partial pair correlation functions for the different measurements are compared in figure 3. The aforementioned shoulder seems to have nearly disappeared for the lower density state, as comparison of the two sets of data by Bellisent *et al* [5] indicates. A serious discrepancy appears in the $g(r)$ calculated on the basis of the data of Howe *et al* [4]: the sharp peak at around

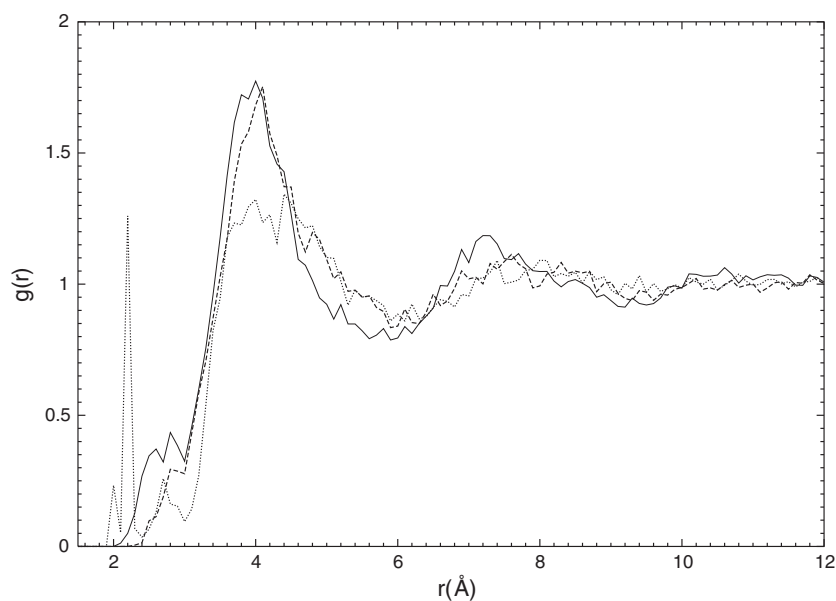


Figure 3. C–C partial pair correlation functions of liquid CO, as obtained from the RMC models based on data in [4, 5] (see text for details). Solid curve: 83.5 K, 4.1 bar; dashed curve: 121.9 K, 23.0 bar; dotted curve: 120 K, 19 bar.

2 Å is necessary for the reproduction of their total structure factor. As was noted by these authors, as well as in [5], this feature may be considered as a manifestation of systematic errors in the data. Since one of the data sets of [5] was obtained for a nearly identical thermodynamical state, CO data from [4] will not be considered further in this work. As data for liquid NO were taken at the same time, under the same conditions, systematic errors of the same level may be expected to be present in those data, as well. (Unfortunately, there is no equivalent of the NO data set available in the literature.)

Molecular centre–molecular centre pair correlation functions are given in figure 4, in comparison with the corresponding hard sphere reference systems. This figure makes it obvious again, that—contrary to what was suggested in, for example, [4]—the structure of liquid CO cannot be approximated by hard sphere systems. It may also be stated that—in accordance with a suggestion by Bellisent *et al* [5]—the structure at the higher density shows similar features to that of liquid nitrogen. For instance, there seems to be a clear long range correlation, extending out to at least the third maximum, between positions of molecular centres, just as in liquid N₂ [15, 16]. These longer range correlations seem to be smeared out as the density is lowered.

Functions characterizing particular molecular orientational correlations in liquid CO are given in figure 5. First of all, it is clear that, especially at the higher density, the microscopic arrangement of neighbouring molecules cannot be called ‘hard sphere like’ (random). We stress that this finding is in contradiction to what has been suggested earlier. What may have led to the misinterpretation of experimental data is the lack of suitable 3D models during the earlier studies; studying all (or at least, more) aspects/projections of ‘the structure’ could not be carried out without the models.

As may have been suspected on the basis of the close similarity of partial pair correlation functions, the direction of the molecules seems to play no role in determining local arrangements; for instance, ‘parallel’ and ‘antiparallel’ configurations occur with roughly

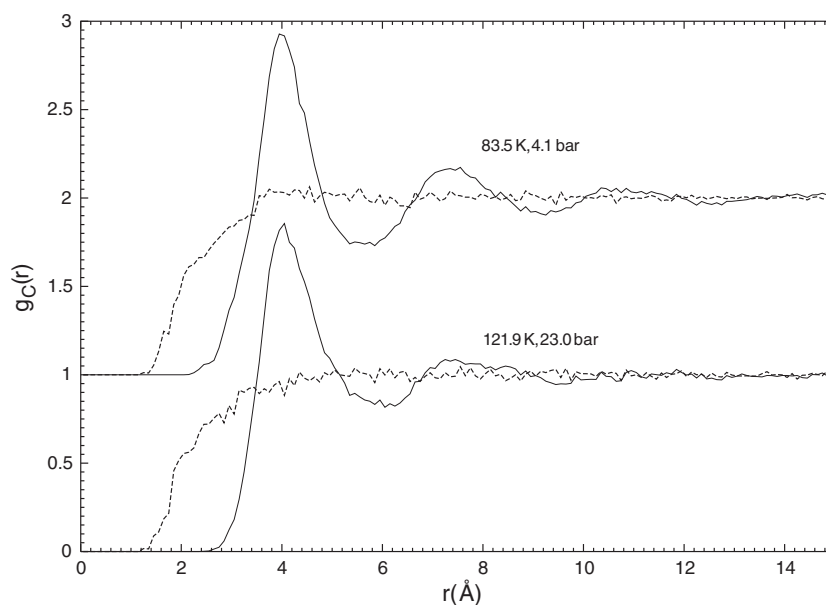


Figure 4. Molecular centre pair correlation functions of liquid CO. Solid curves: RMC models; dashed curves: hard sphere reference systems. (The curve pairs are shifted along the y-axis by 0 and 1.0, respectively.)

the same frequency. Of the particular type of mutual arrangements studied here, at 85.3 K, ‘T-shaped’ ones clearly dominate at the lowest r values that could be considered, up to about 3.5 Å (minimum distance for reasonable statistics: about 3 Å). These almost contacting ‘T-shaped’ pairs may be responsible for the small shoulder on the low- r side of the ppcfs (see figure 2). Next, up to about the position of the first maximum of the centre pair correlation function (4 Å), ‘parallel’ arrangements become important (minimum distance for acceptable statistics: about 3.5 Å). The clarity of specific orientations decreases beyond 4 Å; ‘T-shaped’ and ‘chain-like’ arrangements have slightly higher weights than average, perhaps up to the position of the first minimum of the centre pair correlation function. Beyond 6 Å, no clear sign of orientational correlations can be seen.

Orientalional correlation, similarly to other characteristics, indicates a significantly more disordered structure at 121.9 K. The most distinct feature is the relatively high abundance of ‘parallel’ (and ‘antiparallel’ and ‘cross-like’: these are members of the same group) mutual orientations between 3.5 and 4.0 Å. Much fewer ‘T-shaped’ pairs form here than at 83.5 K and they are further apart (about 3.5 Å); this is why there is no shoulder on the low- r side of the ppcfs (cf figure 3). (Note that some of the large values at the lowest distances are misleading: for reasonable statistics, the minimum distance between pairs of molecules is about 3.5 Å, considerably higher than it was for the denser liquid.)

3.2. Liquid nitric oxide

Experimental and RMC model total structure factors for liquid nitric oxide, at two isotopic compositions, are compared in figure 6. Note that for achieving the level of agreement shown in the figure, an extra feature of the RMC code, the possibility of subtracting sloping/quadratic backgrounds, had to be made use of. It is clear that the introduction of the coordination

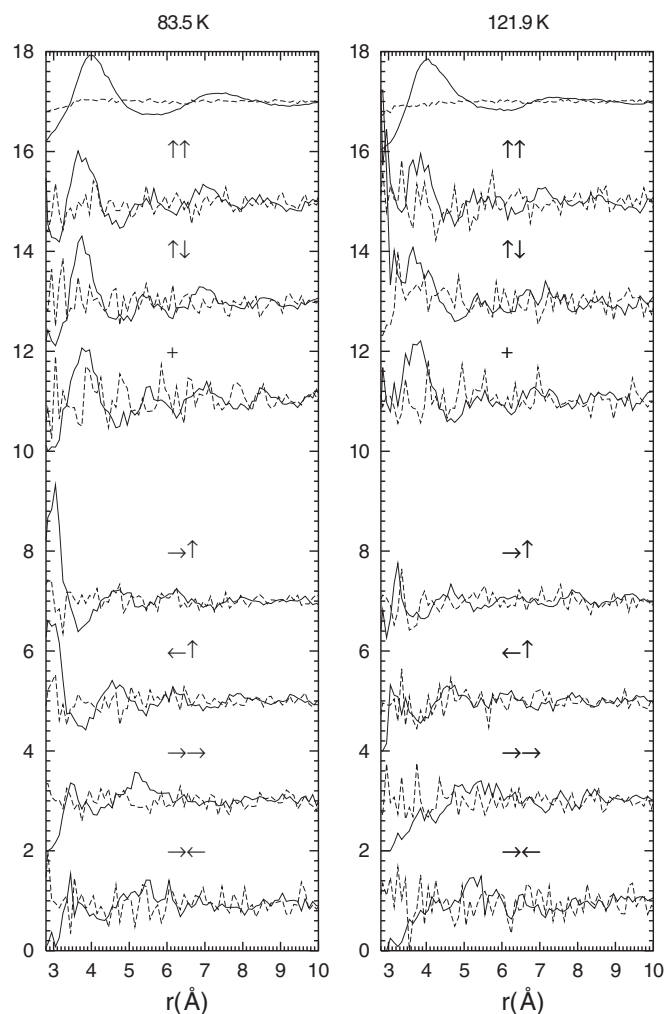


Figure 5. Orientational correlations in liquid CO. Solid curves: RMC models; dashed curves: hard sphere reference systems. The arrows, that symbolize CO molecules, point from the C atoms towards the O atoms. The centre–centre correlation functions are also shown for comparison (uppermost curves). (The curve pairs are shifted along the y-axis by 0, 2, 4, 6, 10, 12, 14 and 16, respectively.)

constraint (on the $N \cdots N$ intermolecular coordination) has not deteriorated the quality of the fit. On the other hand, if an additional constraint on the $O \cdots O$ intermolecular distance is introduced (which would enforce the formation of ‘cis-planar’ shaped dimers) then it is not possible to fit the data at all. This has to be taken as an indication that these diffraction data, which happen to be the only ones on the liquid phase of NO, are not consistent with that particular dimer structure.

Partial pair correlation functions for the ‘unconstrained’ model are shown in figure 7. The N – N partial behaves very differently from the other two: it has a strong peak at 2.4 Å. This peak is characteristic of the intra-dimer $N \cdots N$ distance; the fact that it appears only on the N – N partial indicates that the set of two total structure factors, in combination with RMC, may be sufficient for a reliable separation of the ppcfs. Note also that, for the magnitude of the neutron

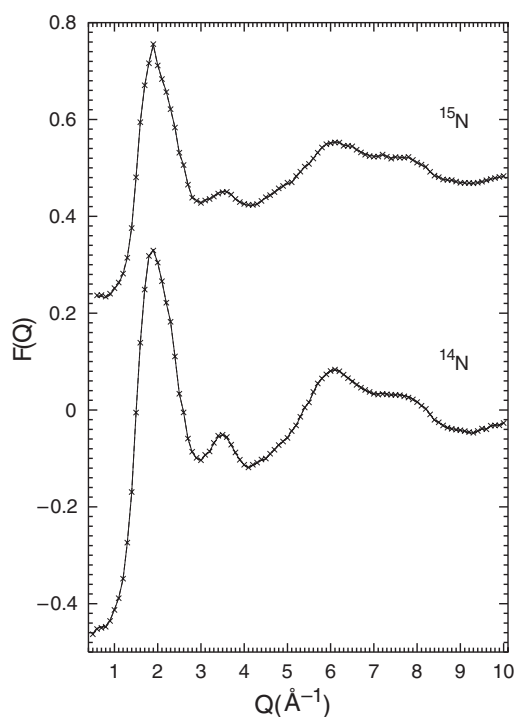


Figure 6. Experimental [4] (symbols) and RMC fitted (solid curve) structure factors of liquid nitric oxide at 120 K. Curves for constrained calculations are also shown (dashed curves). (The curve pairs are shifted along the y-axis by 0 and 0.5, respectively.)

weighting factors (N–N: 0.22/0.10, N–O: 0.27/0.19 and O–O: 0.08/0.08 for samples containing $^{14}\text{N}/^{15}\text{N}$), it is the N–N partial that is sampled the best in a neutron diffraction experiment. For a better determination of the O–O contribution, one may turn to x-ray diffraction (where the O–O weight would be larger than the N–N one, since O has more electrons than N). The $\text{N} \cdots \text{N}$ intra-dimer peak gets somewhat stronger when the coordination constraint is turned on; however, the increase is not very big, indicating that the unconstrained model contains the basic features. The small intensities between the intramolecular N–O and the intermolecular $\text{N} \cdots \text{N}$ peaks are considered as artefacts, possibly indicating the level of systematic errors.

Molecular centre pair correlation functions for liquid NO are compared to those obtained for reference hard sphere systems in figure 8. Hard spheres are not a suitable model for the description of this liquid, either. What is interesting to observe, however, is that the range of correlations between molecular centre positions is much shorter (extending not really beyond the first minimum) than it was in liquid CO.

Oriental correlations are characterized in figure 9, for both the unconstrained and constrained RMC models. It is obvious that, in some cases, the introduction of the constraint has a dramatic effect on the mutual orientations: one example, where it is almost certainly unphysical, is the huge increase of ‘chain-like’ arrangements. Functions that remain stable over switching on the constraint are more suitable for describing what the real microscopic structure might be. One such example is one of the ‘T-shaped’ configurations that seems to be dominant around 3 Å (the minimum distance for acceptable statistics is about 2.65 Å in this case). Another stable feature is the abundance of ‘parallel’ pairs. This observation deserves some

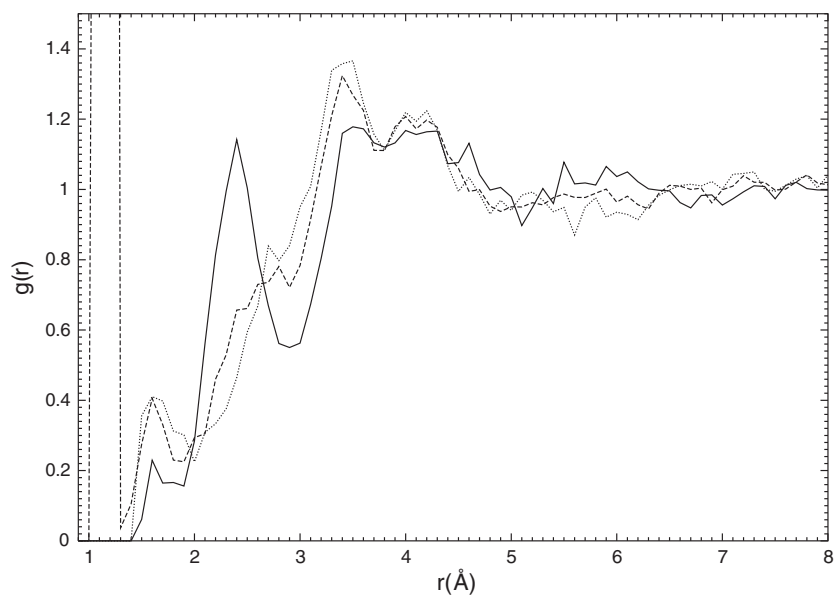


Figure 7. Partial pair correlation functions of liquid NO at 120 K, as calculated from the unconstrained RMC model. Solid curve: N–N; dashed curve: N–O; dotted curve: O–O.

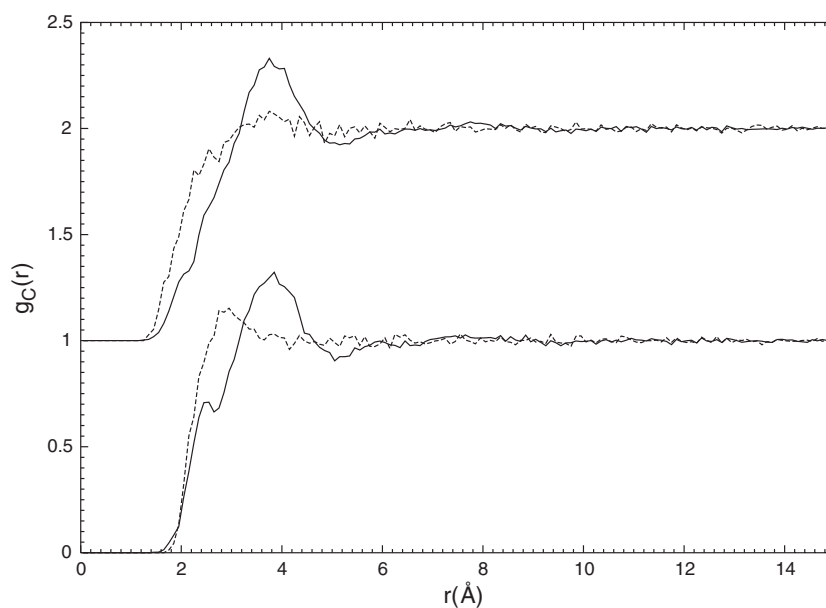


Figure 8. Molecular centre pair correlation functions of liquid NO. Above: unconstrained model. Below: constrained model. Solid curves: RMC models; dashed curves: hard sphere reference systems. (The curve pairs are shifted along the y -axis by 0 and 1.0, respectively.)

more attention since if ‘cis-planar’ shaped dimers were formed then the number of ‘parallel’ orientations should increase. This does not happen, which serves as a further argument against the dominance (and moreover, even against the existence) of ‘cis-planar’ dimers. What is also

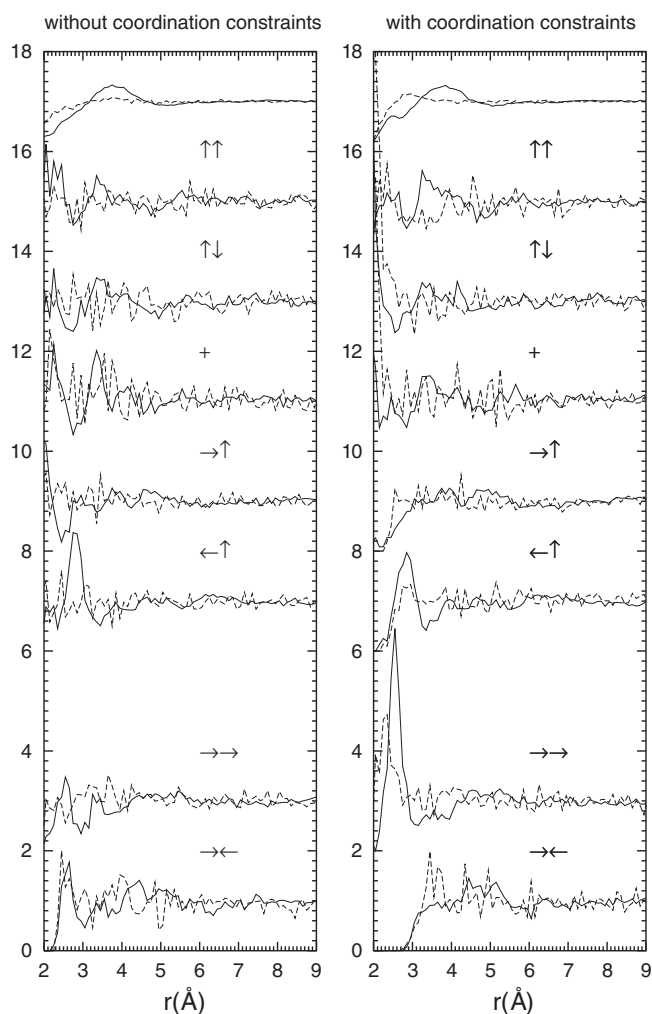


Figure 9. Orientational correlations in liquid NO. Solid curves: RMC models; dashed curves: hard sphere reference systems. The arrows, that symbolize NO molecules, point from the N atoms towards the O atoms. The centre-centre correlation functions are also shown for comparison (uppermost curves). (The curve pairs are shifted along the y-axis by 0, 2, 6, 8, 10, 12, 14 and 16, respectively.)

worthwhile noting is that for NO, the direction of the molecule does count: for instance, the two possible ‘T-shaped’ configurations (see figure 9) are no longer equivalent.

4. Conclusions

Based on large structural models that are fully consistent with experimental structure factors of liquid carbon monoxide, it could be established that, surprisingly, there are well defined orientational correlations in this liquid, particularly at the higher density. A transition from the dominance of ‘T-shaped’ configurations to mostly ‘parallel’ ones could clearly observed below and around the first maximum of the molecular centre-molecular centre pair correlation function.

Liquid nitric oxide exhibits much shorter ranged centre–centre correlations than found in liquid CO. There is only one popular orientation, one of the two ‘T-shaped’ variations that maintained its importance as the coordination constraint was switched on. The existence of dimers, up to 90% of the monomers, was found to be consistent with diffraction results. On the other hand, no significant proportion of ‘cis-planar’ type dimers is supported by the data of Howe *et al* [4].

Acknowledgments

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