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Orientational correlations in high-pressure fluid oxygen and nitrogen

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High-pressure x-ray diffraction measurements for supercritical fluid oxygen at 0.9, 1.2, 4.3, and 5.2 GPa and for supercritical fluid nitrogen at 2.5 GPa have been carried out at room temperature by using synchrotron x-ray diffraction. The structure factors have been interpreted by means of the reverse Monte Carlo method. Site-site and center-center radial distribution functions and relative orientations of molecular axes as a function of distance between molecular centers have been calculated from the particle configurations. At distances below the position of the first maximum of the center-center radial distribution function, the dominance of parallel and "X-shaped" alignments of neighboring molecules has been revealed. Superfluid O_2 was found to display considerably stronger orientational correlations than N_2. Structural differences between oxygen at 4.3 and 1.2 GPa can be explained by the different densities of these systems.

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I. INTRODUCTION

Diffraction studies of the liquid structure at high pressures have led to a much improved understanding of the properties of materials in general.[1–4] New phenomena, such as the liquid-liquid phase transition in a one-component material, phosphorus,[1] have been found. Investigations at gigapascal pressures, however, pose extreme difficulties during the experiment, as well as while processing raw data; for this reason, complicated methods of diffraction data analyses had to be introduced.[3]

The structure of the high-pressure phases of oxygen, the most abundant element on Earth, has been extensively studied over the past decades.[5–7] These investigations have been aimed at determining the structure of crystalline phases. Concerning fluid phases at high pressure, it has been known for quite a long time that oxygen has an anomalously high crystallization pressure, about 5.9 GPa, at room temperature whereas nitrogen crystallizes just above 2.5 GPa.[8,9] Although spectroscopic data are available on high-pressure liquid oxygen and nitrogen,[9,10] the structure of fluid oxygen and nitrogen has not been studied just below the crystallization pressure at room temperature. For the "normal," low-temperature, liquid phases diffraction data are available.[11,12] Very recently, an x-ray diffraction study of fluid oxygen has been reported for states between 357 K, 7.4 GPa and 750 K, 17.2 GPa;[13] unfortunately, the issue of orientational correlations has not been addressed there.

As for theory/computer simulation, high level *ab initio* molecular-dynamics (MD) studies for both the low-temperature liquid[14] and the high-temperature supercritical fluid and solid phases[15] have been conducted; the—experimentally easier to maintain—room temperature, high-pressure fluid phases have not yet been considered. Investigation of the "intermediate" thermodynamic states was therefore rather timely. The purpose of the present study is to provide these missing experimental data on the structure of high-pressure phases of oxygen and nitrogen.

II. EXPERIMENTAL

X-ray diffraction experiments were conducted using the high-energy x-ray diffraction beamline BL04B2 (Ref. 16) at the SPring-8 synchrotron radiation facility (Japan). The energy of the (focused, 40 μm wide) monochromatic x-ray beam was 37.6 keV. For improving counting statistics, an imaging plate detector was used. Sample loading was carried out by compression and oxygen and nitrogen acted as their own pressure media. The diffraction patterns of fluid samples were measured in a diamond-anvil cell (DAC) at pressures of 2.5 GPa (fluid N_2), 0.9, 1.2, 4.3, and 5.2 GPa (fluid O_2). The number densities of these samples were 0.0602, 0.0531, 0.0568, 0.0768, and 0.0806 $Å^{-3}$, respectively. Despite the difficult experimental conditions, a scattering variable range of up to between 9 (nitrogen) and 11 (oxygen at 1.2 GPa) $Å^{-1}$ could be covered with the required accuracy. Raw data were corrected by the usual methods,[17] with a special attention to the subtraction of the scattering from the DAC. Detailed description of data acquisition and data handling at the high-pressure setup of BL04B2 can be found in a recent publication.[18]

Resulting "total scattering" structure factors (sfs), $F(Q)$, are shown in Fig. 1 for oxygen at each pressure value, whereas $F(Q)$ for fluid nitrogen is given by Fig. 2 (for an exact definition of $F(Q)$, see Ref. 19). Note that for oxygen, structure factors at 0.9 and 1.2 are rather similar, just as they are at 4.3 and 5.2 GPa; for this reason, structural modeling (see below) was carried out only at 1.2 and 4.3 GPa.

Since direct Fourier transformation to r space would be prone to truncation errors (cf. the relatively low maximum

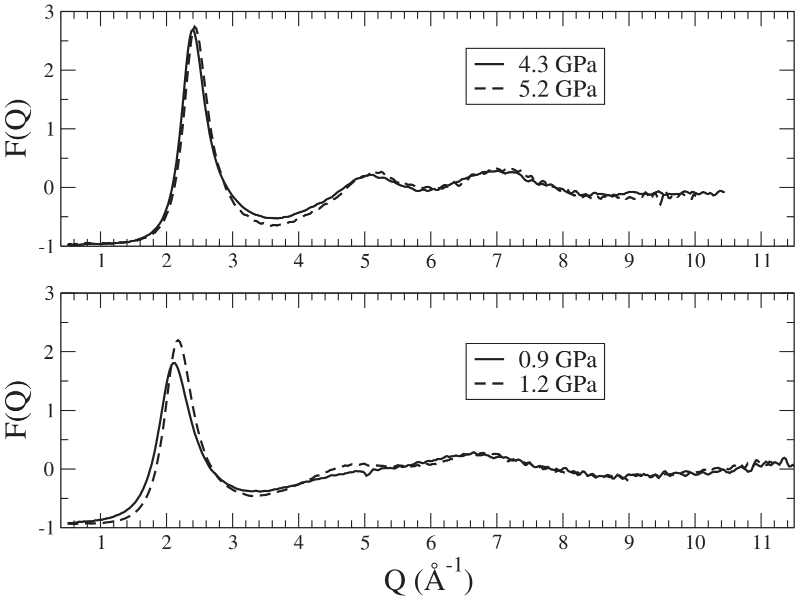

FIG. 1. Experimental structure factors for high-pressure fluid phases of oxygen. The lower and higher pressure curves are given in different panels.

values of the scattering variable, Q), it is safer to apply an inverse method for the transition to real space. One of the possibilities is the application of the reverse Monte Carlo (RMC) method,[20] which is also capable of providing large structural models that are consistent with the measured sfs. Details of the RMC method can be found in several publications,[20–23] so that only specifications for the current calculations are given here.

III. REVERSE MONTE CARLO CALCULATIONS

In each case, 5000 molecules (10000 atoms) were put in cubic boxes. In each simulation, several hundreds of successful moves/atom were completed. Molecules were flexible, which was made possible by the application of "fixed neighbor constraints" (fncs).[21,23] The intramolecular N–N and O–O bonds were allowed to vary between 1.05–1.15 and 1.15–1.25 Å, respectively. Calculations were conducted by the RMC++ software.[21]

Hard-sphere Monte Carlo calculations of molecular assemblies, with the same parameters (density, bond-length constraints, cutoffs) as the RMC runs, have also been carried out for the three systems. These calculations provided reference structures which possess all features that originate to excluded volume (pure steric) effects. Differences between hard sphere and RMC structures are characteristic to the nature of intermolecular interactions. This—rather simple—way of interpreting diffraction results and corresponding RMC models proved to be outstandingly helpful previously.[24,25]

Distance dependent orientational correlation functions were determined the same way as described in Ref. 24. In short, angles confined by the molecular axes and the line connecting molecular centers have been found. For any given pair of molecules, two such angles exist. With the help

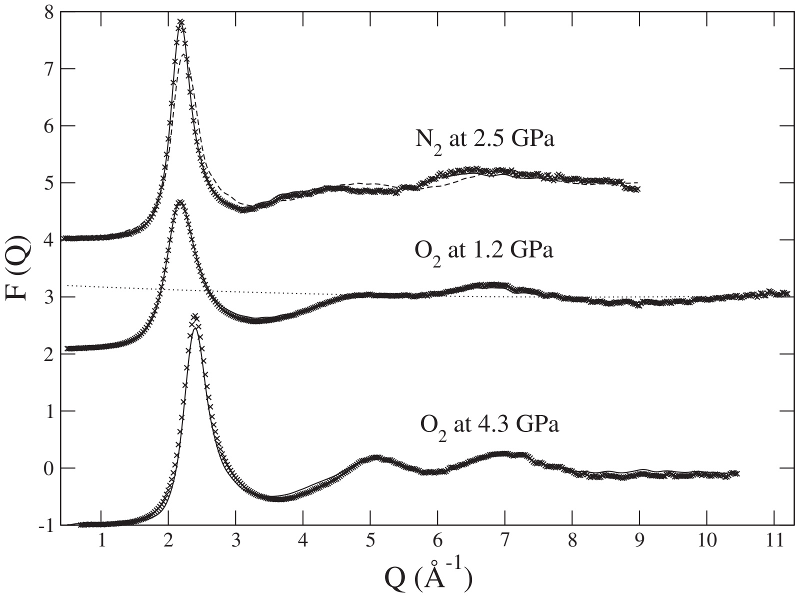

FIG. 2. Experimental (symbols) and RMC simulated (solid line) structure factors for high-pressure fluid phases of nitrogen and oxygen. For fluid nitrogen at 2.5 GPa, results for the highest packing fraction reference (hard-sphere) system are also shown (dashed line). The quadratic background refined by RMC modeling is shown for the 1.2 GPa oxygen tsf (dotted line).

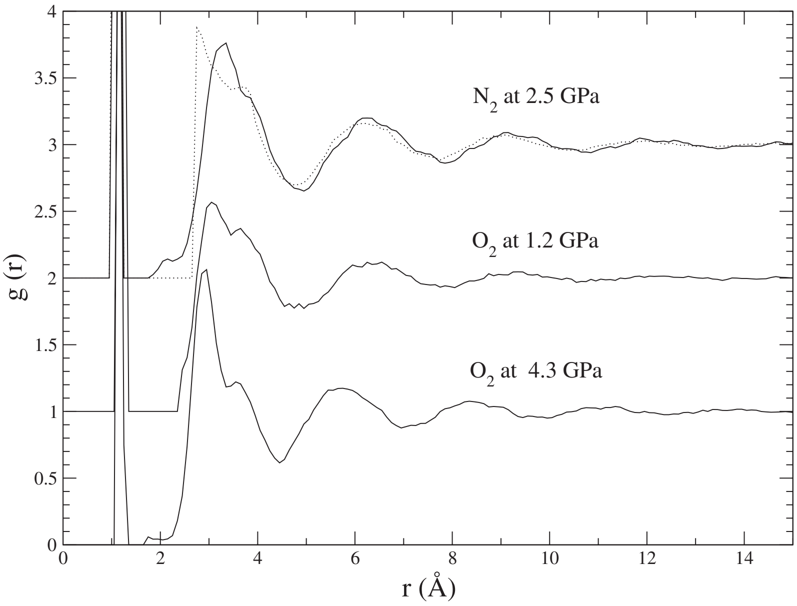

FIG. 3. Site-site radial distribution functions of high-pressure fluid nitrogen and oxygen, as obtained directly from particle coordinates (solid lines). For fluid nitrogen at 2.5 GPa, results for the highest packing fraction reference (hard-sphere) system are also shown (dashed line).

of an additional angle, confined by the two molecular axes, any given popular mutual orientation of two molecules, such as "parallel," "X (cross) shaped," "T shaped," or "chainlike," 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 configurations have been calculated as a function of the distance between molecular centers. 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 center-center 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, orientational correlation functions are shown from 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.

IV. RESULTS AND DISCUSSION

Figure 2 compares experimental structure factors for the high-pressure states to the $F(Q)$'s of the corresponding RMC models. Reproduction of experimental data may be termed as very good in each case. We note that for achieving such a level of consistency with measurement, a particular feature of the RMC++ software, the possibility of refining a—small—quadratic background for the experimental sfs, had to be exploited. This step was necessitated by the extreme experimental conditions for which the standard data processing software[17] cannot be made fully prepared. The quadratic background refined by RMC++ is shown in Fig. 2 for the 1.2 GPa oxygen data, where the data could not be approached without the quadratic term.

Site-site radial distribution functions (ssrdfs), $g(r)$, as calculated directly from particle configurations, are shown in Fig. 3. It is obvious that, due to the application of an inverse method for the transition from Q to r space, no truncation errors are present in any of the ssrdfs. The most apparent feature of these functions is the characteristic shoulder on the higher r side of the first intermolecular peak that appears around (or a little above) 3.5 Å for each system; this "double-peak" shape of the first intermolecular maximum was not found by *ab initio* MD either at atmospheric[14] or higher than 25 GPa[15] pressures. The origin of these shoulders can most certainly be found in terms of specific local orientations of molecular axes, whose orientations will be scrutinized below.

There is, however, one more point worth emphasizing here, concerning the *position* of the first intermolecular maximum of ssrdfs. The maximum positions are 3.4, 3.1, and 3.0 Å for the 2.5 GPa N_2, 1.2 GPa O_2, and 4.3 GPa O_2 systems, respectively. What is noteworthy here is that despite the fact that the N_2 molecule is smaller (with a shorter intramolecular distance) than the O_2 molecule, it is the oxygen molecules that approach each other to a considerably shorter distance. This is a strong indication for that attractive forces between O_2 molecules are stronger than those acting between N_2 molecules. It is also interesting to note that this—admittedly, not entirely unexpected—finding follows directly from (a comparison of) diffraction data sets.

Molecular center-molecular center radial distribution functions (ccrdfs), $g_{CC}(r)$, are shown in Fig. 4. The curves are similar to the rdfs of a simple liquid (for instance, of liquid argon[20]). Oscillations above 15 Å can only be observed for the 2.5 GPa nitrogen fluid; this indicates that the nitrogen molecule is more spherical than the oxygen molecule. Maximum positions show a similar trend as observed for the ssrdf's, although differences here are smaller.

$g_{CC}(r)$'s, being functions with a simple shape, provide a good opportunity for a detailed comparison with reference hard-sphere (HSMC) systems. As is obvious from Fig. 4, if

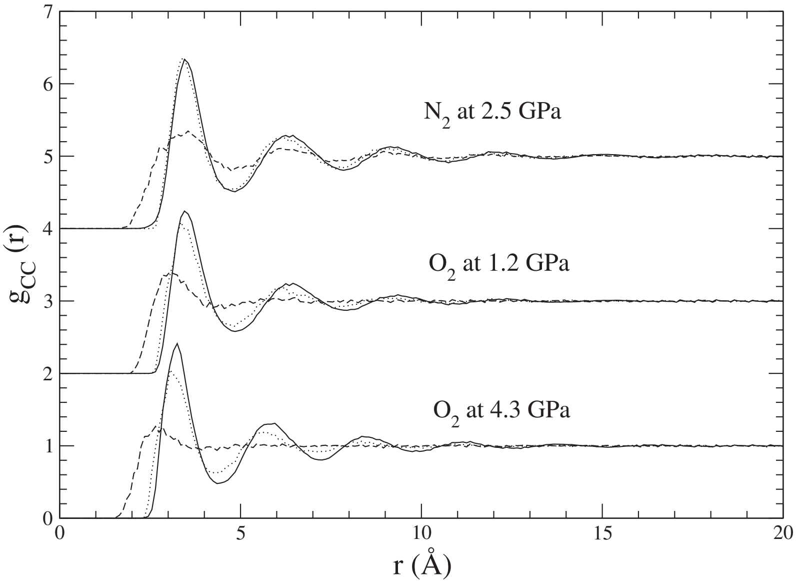

FIG. 4. Center-center radial distribution functions of high-pressure fluid nitrogen and oxygen, as obtained directly from particle coordinates (solid lines). Results for the lowest (dashed lines) and highest (dotted lines) packing fraction reference (hard-sphere) systems are also shown. (See text for details.)

identical particle sizes are used in RMC and HSMC calculations then ccrdf's for the reference systems are much more disordered then those for the "real" (RMC) systems. The difference between curves obtained from RMC and HSMC may be taken as an indication that steric effects cannot explain even the simplest structural feature of these molecular liquids directly. If, however, particle sizes are increased in the hard-sphere Monte Carlo calculations to the highest values allowed by the density (cutoffs 2.7, 2.7, and 2.45 Å for the "HSMC replicas" of the 2.5 GPa N_2, 1.2 GPa O_2, and 4.3 GPa O_2 systems, respectively), so that particles can still be moved around, then agreement between RMC and HSMC results becomes (in the worst case, only nearly) quantitative at the $g_{CC}(r)$ level. We stress that particle sizes necessary for achieving such a level of agreement are unrealistically large (for a more detailed discussion of this point, see below).

We now turn to our main subject, the description of orientational correlations found in the high-pressure (supercritical) fluid phases of nitrogen and oxygen. Figure 5 summarizes results obtained for the three measurements. It may be useful to note in advance that up to the first maximum of $g_{CC}(r)$, the number of molecular pairs that could be categorized as realizing one of the specific ("ordered") orientations considered here was somewhat higher than two times the number expected from random orientations. In other words, the number of "regular" pairs in this distance region was more than 25% of all pairs.

The most striking features are undoubtedly the very strong peaks of the orientational correlation functions representing the parallel and the X-shaped arrangements at the closest distances, up to about 3.5 Å, whose distance corresponds (roughly) to the first peak position of $g_{CC}(r)$ for each systems studied here. It is immediately apparent that these, parallel and X-shaped, correlations for oxygen (at both pressures) are much stronger than they are for nitrogen. It is now possible to provide an explanation for the formation of the

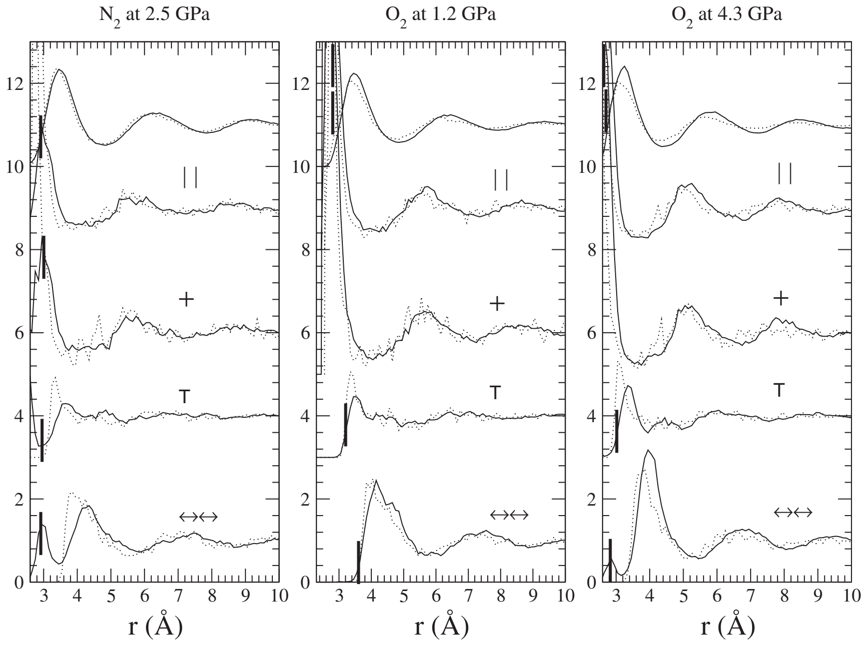

FIG. 5. Orientational correlation functions for high-pressure fluid nitrogen and oxygen, as obtained directly from particle coordinates (solid lines). Results for the highest packing fraction reference (hard-sphere) system are also shown (dotted lines). The center-center correlation functions are also 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.)

double first intermolecular peak of the site-site rdfs (Fig. 3): at nearly the same center-center distance, parallel and X-shaped mutual orientations are equally possible, giving rise to only slightly different site-site distances. Parallel orientations belong to the shorter distances, whereas X-shaped orientations contribute primarily to the strong shoulder (or high r region of the double peak).

Recent molecular-dynamics simulation studies[14] on the normal liquid phase (low temperature, atmospheric pressure) also show the importance of the parallel ("H" type, according to the terminology of Ref. 14) but not of the X-shaped ("b" in Fig. 3 of Ref. 14) alignment. Consistent with this finding, the ssrdf of Ref. 14 does not exhibit a double first intermolecular maximum. It may also be noted that the high number of parallel and cross-shaped pairs found in the present study is consistent with the presence of O_4 units, suggested by Oda *et al.*;[14] based on the static structure only, however, stronger statements cannot be made.

Interestingly, chainlike orientations become important in high-pressure fluid oxygen, particularly at 4.3 GPa, in the region following the first maximum of $g_{CC}(r)$, at around 4 Å. This feature is quite unique, not found for either liquid CO and NO (which have similar molecular size) via similar analyses as done here[24] or by *ab initio* molecular dynamics for liquid O_2 at ambient pressure.[14] T-shaped arrangements have no significance in either high-pressure nitrogen or oxygen.

We have made an attempt to identify the origin of the orientational correlations found in the high-pressure fluid phases. To investigate if excluded volume effects (density, particle size)—as may be expected for simple liquids—are mainly responsible for the correlations, series of reference (HSMC) systems have been generated for each sample. The packing fraction within the series was varied, by varying the (intermolecular) cutoff value (i.e., the size of the atoms). The smallest packing fraction value, between 15% and 20%, always corresponded to the cutoff value used in the RMC calculations, whereas the largest one, between 45% and 49%, was the largest achievable at all under the present circumstances (within a reasonable amount of time). It was obvious (as indicated for the case of the center-center correlation function, see Fig. 4) that cutoffs used in the RMC calculations result in too high a level of disorder in the HSMC models, with largely uncorrelated orientations. Using packing fraction values that may be considered as characteristic to the real systems (36%, 35%, and 37% for nitrogen at 2.5 GPa and oxygen at 1.2 and 4.3 GPa, respectively; estimated from the onset of the site-site rdfs) still provides too low a level of orientational ordering. Only the largest manageable cutoffs (and thus, packing fraction values) provide semiquantitative agreement with radial distribution functions (see Figs. 3 and 4) and orientational correlation functions (cf. Fig. 5) found for the real systems (represented by RMC structural models). Note that these highest packing fraction values (above 45%) are far too high to be realistic; that is, by no means would it be justified to conclude that pure steric effects were responsible for orientational correlations found in these high-pressure fluids.

On the other hand, it seems that the real systems realize orientational correlations (and in general, real-space structural characteristics, see Figs. 3 and 4) that are inherent to the "frozen" HSMC systems. In other words, the *character* of orientational correlations found in high-pressure fluid nitrogen and oxygen resembles that featuring hard- (fused-) sphere reference systems; the *extent* of these correlations is, on the other hand, very different. From this finding, it may be conjectured that correlations between magnetic moments of O_2 molecules do not bring about specific orientational forces (even though the strength of interactions between molecules is obviously influenced by magnetic properties).

It may also be interesting to note that it is the high-pressure nitrogen data that can be best described on the basis of the HSMC reference system (see particularly Fig. 4); that is, out of the materials considered here, nitrogen at 2.5 GPa resembles a hard-sphere liquid the most. This is consistent with the suggestion[9] that intermolecular interactions are stronger in fluid O_2 than in N_2 (cf. also discussions above, concerning radial distribution functions) and may be taken as an explanation for the abnormally high solidification pressure of fluid oxygen.

V. CONCLUSIONS

In conclusion, we have performed x-ray diffraction experiments on high-pressure fluid nitrogen (at 2.5 GPa) and oxygen (at 0.9, 1.2, 4.3, and 5.2 GPa). Site-site and center-center radial distribution function, as well as distance dependent orientational correlations have been determined by using reverse Monte Carlo modeling. It could be established that well defined orientational correlations exist in all of the materials, particularly below about 3.5 Å. In agreement with *ab initio* MD simulations,[14] the dominant mutual arrangement of O_2 molecules appears to be the parallel one; here, however, the importance of X shaped and (for the higher density oxygen sample, at larger intermolecular distances) chainlike alignments has also been revealed. It is expected that the present results will boast high level computer simulation studies, aiming at a detailed understanding of the microscopic behavior of high-pressure condensed phases of oxygen.

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