

Orientational Correlations in High-Pressure Fluid Oxygen and Nitrogen

Diffraction studies of the liquid structure at high pressures have led to a much improved understanding of the properties of materials in general. New phenomena, like the liquid-liquid phase transition in phosphorus, have been found. Investigations at GPa pressures, however, pose extreme difficulties during the experiment, as well as while processing raw data.

The structure of the high-pressure phases of oxygen, most abundant element on Earth, has been studied experimentally over the past. These investigations have aimed at determining the structure of crystalline phases, sometimes at extremely high pressure [1]. 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. The structure of fluid oxygen and nitrogen has not yet been studied by diffraction methods just below the crystallization pressure. The purpose of the present study [2] was to provide this missing piece of experimental information and furthermore, to understand the –disordered– fluid structure.

X-ray diffraction experiments were conducted using the high-energy X-ray diffraction beamline **BL04B2**. The energy of the (focused, 40 micron 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 N₂), 0.9, 1.2, 4.3 and 5.2 GPa (fluid O₂). Raw data were corrected by usual methods, with a special attention to the subtraction of the scattering from the DAC.

Resulting 'total scattering' structure factors (sf), $F(Q)$, are shown in **Fig. 1** for fluid oxygen and nitrogen. Note that for oxygen, structure factors at 0.9 and 1.2 GPa 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, 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 [3], which is also capable of providing large structural models that are consistent with the measured sf. In each RMC calculation, 5000 molecules were put in cubic boxes and several hundreds of successful moves/atom were completed.

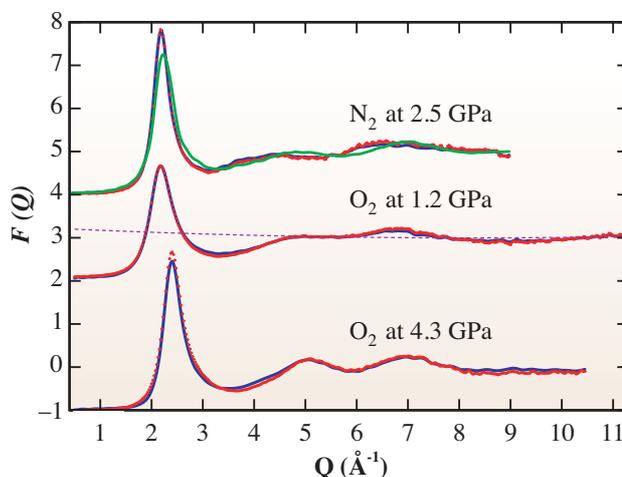


Fig. 1. Experimental (red dots) and RMC simulated (blue line) structure factors for high-pressure fluid phases of nitrogen and oxygen. For fluid nitrogen at 2.5 GPa, results for the highest packing fraction reference (hard sphere) system are also shown (green line). The quadratic background refined by RMC modeling is shown for the 1.2 GPa oxygen sf (magenta dotted line).

Calculations were conducted by the RMC++ software [4]. Hard sphere Monte Carlo (HSMC) calculations of molecular assemblies, with the same parameters (density; bond-length constraints) 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.

Figure 1 compares experimental structure factors to $F(Q)$'s of the corresponding RMC models. For achieving such a level of consistency with experiment, a particular feature of the RMC++ software, the possibility of refining a –small– quadratic background for the experimental sf, had to be exploited. This step was necessitated by the extreme experimental conditions for which the standard data processing software cannot be made fully prepared.

Distance dependent orientational correlation functions were determined in terms of easy-to-understand mutual orientations of two molecules, as depicted by **Fig. 2**. As it is explained in the figure, 'parallel', 'X(cross)-shaped', 'T-shaped', or 'chain-like', have been considered. The ratio of 'regular' pairs, which could be categorized according to the 4 specific arrangements shown in **Fig. 2**, was more than 25% of all pairs found below 3.5 Å. **Figure 3** summarizes results obtained for the three systems. 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. 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 could also be shown (*c.f.* Fig. 3) that the real systems realize orientational correlations 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 to that featuring hard sphere reference systems; the *extent* of these correlations is, on the other hand, different. From this finding it may be conjectured that correlations between magnetic moments of O₂ molecules do not bring about specific orientational forces.

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) [2]. Site-site and center-center radial distribution functions, as well as distance dependent orientational correlations have been determined by using RMC modeling. Well defined orientational correlations were found in all of the

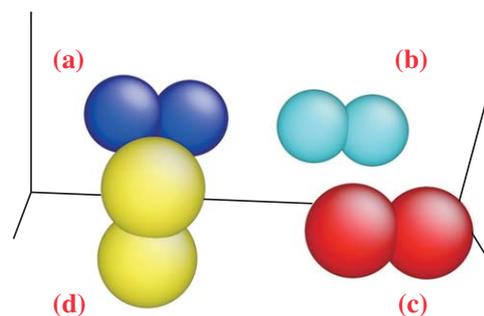


Fig. 2. Specific orientations of molecular pairs considered in this work. (a)-(b): chain-like configuration; (b)-(c): parallel configuration; (c)-(d): T-shaped configuration; (d)-(a): X-shaped configuration.

materials, particularly below about 3.5 Å. In agreement with *ab initio* molecular dynamics simulations [5] (conducted for lower temperature and pressure), the dominant mutual arrangement of O₂ molecules appears to be the parallel one. Here, however, the importance of 'X-shaped' configurations 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.

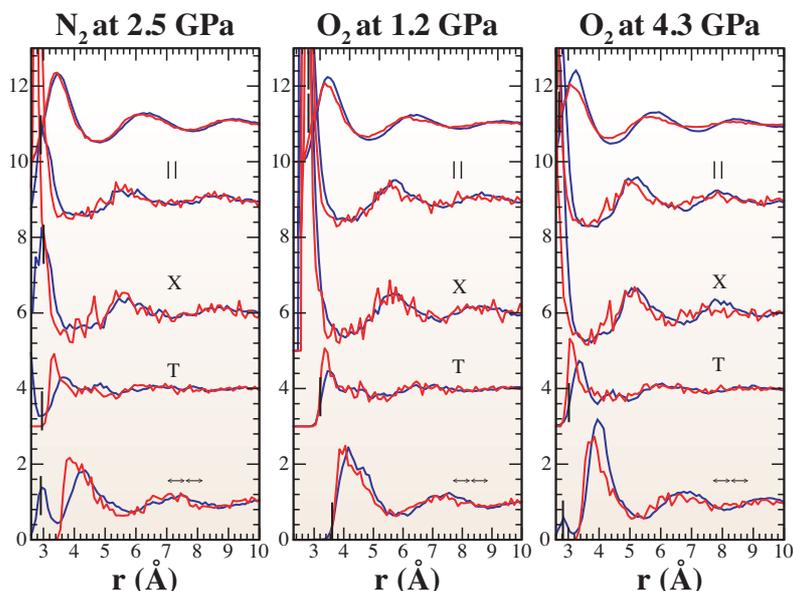


Fig. 3. Orientational correlation functions for high pressure fluid nitrogen and oxygen, as obtained directly from particle coordinates (red lines). Results for the highest packing fraction reference (hard sphere) system are also shown (blue lines). Center-center correlation functions are also shown 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.)

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References

- [1] H. Fujihisa *et al.*: Phys. Rev. Lett. **97** (2006) 085503.
- [2] L. Temleitner, L. Pusztai, Y. Akahama, H. Kawamura, S. Kohara, Y. Ohishi and M. Takata: Phys. Rev. B **78** (2008) 014205.
- [3] R.L. McGreevy and L. Pusztai: Molec. Simul. **1** (1988) 359.
- [4] G. Evrard and L. Pusztai: J. Phys.: Condens. Matter **17** (2005) S1.
- [5] T. Oda and A. Pasquarello: Phys. Rev. Lett. **89** (2002) 197204.