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Structural and magnetic correlations in liquid oxygen: an *ab initio* molecular dynamics study

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Abstract

We have carried out an *ab initio* molecular dynamics simulation of liquid oxygen, a molecular fluid in which the individual O₂ units carry a molecular magnetic moment. In addition to the atomic and electronic structures, our simulation describes the evolution of the noncollinear magnetic structure. The atomic structure shows a strong preference for parallel alignment of first-neighbour molecules. The magnetic structure shows strong short-range antiferromagnetic correlations, in agreement with spin-polarized neutron diffraction data. The short-range correlations, observed in both the structural and magnetic properties, primarily result from appropriate trajectories of colliding O₂ molecules. Our simulation also reveals the occurrence of several long-living O₄ units which survive for time periods longer than four times the average residence time observed during collisions.

1. Introduction

The occurrence of the O₄ molecular unit has been a long-standing issue in materials science for about ninety years [1]. The O₄ molecule was first proposed to explain magnetic susceptibility data on liquid oxygen [2, 3]. However, the formation of a truly long-living unit in the liquid could not be established and its occurrence has been explained in terms of relatively free motions in which two molecules collide with each other according to appropriate trajectories [4]. The unusual property which characterizes this molecular fluid is that the magnetic moment on each molecule is preserved in the liquid state, giving rise to paramagnetic behaviour [2].

Recently, we developed a generalized *ab initio* molecular dynamics scheme [5] to account for noncollinear magnetic structures [6]. This scheme has the potential to describe simultaneously the time evolution of the atomic, electronic, and magnetic properties.

Applied to small iron clusters, this scheme gave fully relaxed structures showing a noncollinear magnetic structure in particular cases [6]. The present application to liquid oxygen demonstrates that this scheme can also be used to perform constant-temperature molecular dynamics simulations of noncollinear magnetic systems.

2. Model and method

We modelled liquid oxygen by a periodically repeated cubic cell of side 11.4 Å, containing 32 molecules at the experimental density of 1.14 g cm⁻³. To describe valence–core interactions, ultrasoft pseudopotentials were used [7]. We expanded the wavefunctions at the Γ point and the corresponding electron density on plane-wave basis sets, defined by energy cut-offs of 25 and 150 Ryd, respectively [8]. The exchange and correlation energy was described by the generalized gradient approximation proposed by Perdew and Wang (PW91) [9].

We started the simulation from an atomic configuration with random phases for intermolecular vibrations. After a brief annealing cycle, the temperature was fixed at 90 K by switching on thermostats on both nuclear and electronic degrees of freedom [10]. After a thermalization period of 5 ps, the following 14 ps were used to average physical quantities. The evolution of the average mean square displacement was typical of diffusive motion in a liquid, giving an estimate for the diffusion constant of $(2.3 \pm 0.2) \times 10^{-5}$ cm² s⁻¹.

3. Results and discussion

Figure 1 shows the function $4\pi r\rho[g(r) - 1]$, where $g(r)$ is the radial distribution function and ρ the atomic number density [11]. The sharp peak at 1.24 Å corresponds to the intramolecular distance between O atoms. The distribution of intermolecular distances starts at 2.3 Å and shows peaks at 3.6 and 6.8 Å, separated by a minimum at 5.3 Å. The radial distribution in the simulation is found to agree well with the experimental one measured by Clarke *et al* [12], of which it reproduces all the important features. In particular, the shoulder at about 4.1 Å, which results from second-neighbour atoms in first-neighbour molecules, is observed in both the theoretical and experimental curves. The first shell of molecules defined by the first minimum contains 13.0 molecules. An excellent agreement between theory and experiment is also found for the nuclear structure factor $S(Q)$ (not shown), which is directly accessible in an elastic neutron scattering experiment [12–14].

From the analysis of the local structure in the liquid, we found a strong preference for a parallel alignment (H-type configuration) of first-neighbour molecules. In figure 2, we show a snapshot of the simulation. We observed that the rectangular configuration dominates for molecules located within a radius of 3 Å. The occurrence of such short-range structural correlations is confirmed by specific features in $S(Q)$, which can be attributed to intermolecular incoherent scattering.

The simulation shows local magnetic moments rotating without pointing into any preferential direction. This is consistent with paramagnetic behaviour, which results in a vanishing average magnetization in the absence of an external magnetic field. The average total magnetization $|\langle M_{\text{tot}} \rangle|$ was found to be $\sim 0.3 \mu_B$ per cell.

During the simulation, we monitored atomic magnetizations which were obtained by integrating the spin density around each atom within a radius of 0.69 Å. Magnetic moments for atoms belonging to the same molecule were found to be almost parallel, in a ferromagnetic configuration. The magnitudes of the atomic moments are found to be close to $0.8 \mu_B$, to be compared with the half of the molecular moment in the gas phase ($1 \mu_B$). Hence, the O₂

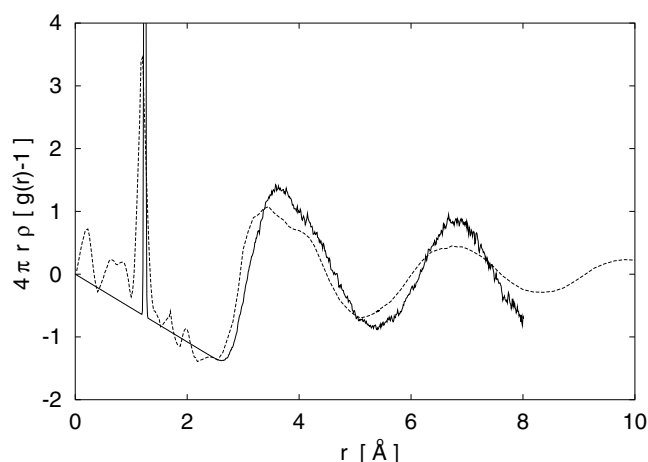


Figure 1. The function $4\pi r\rho[g(r) - 1]$, where $g(r)$ is the radial distribution function and ρ the atomic number density, compared with the corresponding experimental result [12].

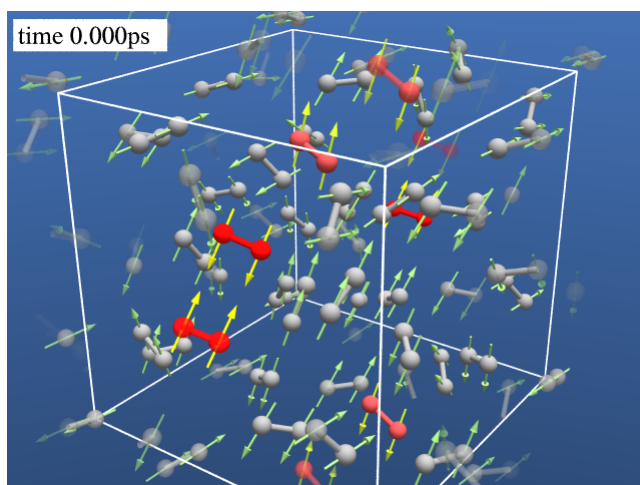


Figure 2. A snapshot taken from the molecular dynamics simulation. The dumb-bell-shaped objects indicate O_2 molecules and the arrows the direction of the magnetization carried by the atoms. A pair of molecules situated within a radius of 3.2 \AA are shown in red. Due to the neglect of spin-orbit coupling, only the relative orientation of the magnetization is meaningful in our simulation.

(This figure is in colour only in the electronic version)

molecules in the liquid preserve to a large extent their individual gas-phase character. This picture is further supported by an analysis of the electronic density of states, which reveals that the electronic energy gap resulting from intramolecular exchange interactions is maintained and that the liquid state only induces some broadening in the molecular energy levels.

As shown in figure 2, the magnetism in our model system clearly presents noncollinear magnetic structures with antiferromagnetic correlations at the short-range distances. To obtain a more detailed description of the magnetic correlations between molecules, we considered

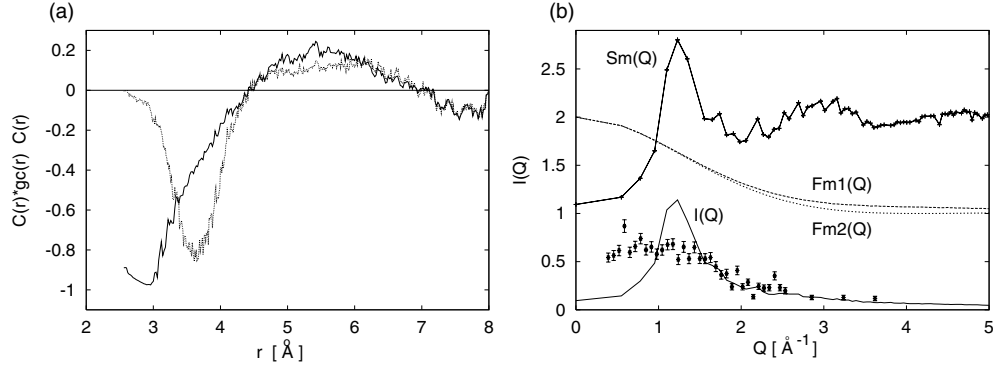


Figure 3. The magnetic structure of liquid oxygen: (a) real-space correlation functions, $C(r)$ (full curve) and $C(r)g_c(r)$ (dotted curve); and (b) magnetic structure factors, $I(Q)$ and $S_m(Q)$, and magnetic form factors, $F_{m1}(Q)$ and $F_{m2}(Q)$ (definitions are given in the text). The points with error bars correspond to experimental data [4]. For clarity, we used in (b) an offset of 1 for $S_m(Q)$, $F_{m1}(Q)$, and $F_{m2}(Q)$.

the magnetic correlation function in real space:

$$C(r) = \frac{\langle \sum_{i \neq j} \mathbf{m}_i \cdot \mathbf{m}_j \delta(r_{ij} - r) \rangle}{\mu^2 \langle \sum_{i \neq j} \delta(r_{ij} - r) \rangle}, \quad (1)$$

where \mathbf{m}_i is the magnetic moment of the i th molecule given by the sum of the respective atomic moments and μ is the average molecular moment. As shown in figure 3(a) [11], the function $C(r)$ shows well defined magnetic correlations. At distances corresponding to nearest-neighbour molecules, antiferromagnetic correlations dominate and appear to saturate for distances lower than 3.1 Å. At larger distances between 4.4 and 7.0 Å, the correlations turn ferromagnetic. By considering the molecular distribution as given by the radial distribution function $g_c(r)$ for molecular centres, we also show in figure 3(a) the product function $C(r)g_c(r)$. The negative peak of $C(r)g_c(r)$ located at 3.7 Å is an indication of antiferromagnetic correlation, and has also been found in the analysis of experimental data [4].

The magnetic structure factor is given by

$$I(Q) = \frac{2}{N\mu_0^2} \left\langle \left| \int d\mathbf{r} \mathbf{m}(\mathbf{r}) \exp(-i\mathbf{Q} \cdot \mathbf{r}) \right|^2 \right\rangle, \quad (2)$$

in which $\mathbf{m}(\mathbf{r})$ is the spin density vector and μ_0 and N are the magnetic moment of an isolated molecule and the number of atoms, respectively. It is useful to express $I(Q)$ in terms of molecular form factors. This can be done under the assumption that the orientation of a pair of molecules is decoupled from the direction of their connecting axis. This gives $I^{\text{approx}}(Q) = F_{m1}(Q) + F_{m2}(Q)[S_m(Q) - 1]$, where $F_{m1}(Q) = \langle |\mu(Q)|^2 \rangle / \mu_0^2$ and $F_{m2}(Q) = |\langle \mu(Q) \rangle|^2 / \mu_0^2$ are molecular magnetic form factors [15], and $S_m(Q) = 2 \langle |\sum_i \mathbf{m}_i e^{-i\mathbf{Q} \cdot \mathbf{r}_i}|^2 \rangle / N\mu_0^2$ is related by Fourier transformation to the real-space correlation $C(r)g_c(r)$ [4]. From the simulation, we obtained both $I(Q)$ and $I^{\text{approx}}(Q)$ and found that the two quantities are hardly distinguishable.

The structure factor $I(Q)$ averaged over configurations in the simulation and the corresponding one measured by means of neutron diffraction [4] are compared in figure 3(b) [11]. Both the theoretical and the experimental $I(Q)$ show a well defined dip around 2 Å^{-1} , while only a shoulder occurs in the experimental $I(Q)$ in correspondence with the large peak at 1.2 Å^{-1} in the calculated $I(Q)$. By separating the contribution to $S_m(Q)$ from

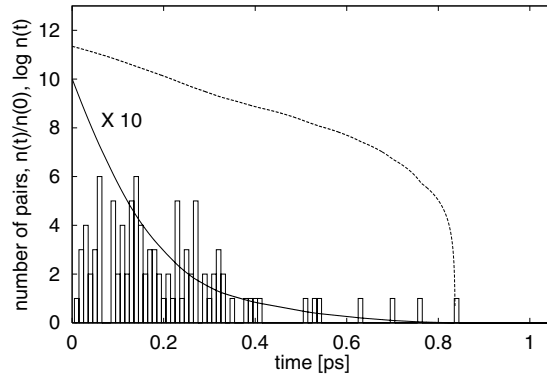


Figure 4. The residence time (histogram) and time distribution function: $n(t)/n(0)$ (full curve) and $\log n(t)$ (dotted curve) for $r_c = 3.1 \text{ \AA}$.

molecules at different distances, we found that the dip around 2 \AA^{-1} originates from short-range antiferromagnetic correlations, whereas the peak at 1.2 \AA^{-1} contains contributions from both antiferromagnetic and ferromagnetic correlations. These results indicate that we can infer the occurrence of short-range antiferromagnetic correlations directly from the experimental data points in Q -space [4]. The differences between the theoretical and experimental $I(Q)$ for $Q < 1.4 \text{ \AA}^{-1}$ result from the neglect of thermal electronic excitations in the simulation, as a consequence of the use of the Born–Oppenheimer approximation [5]. In fact, note that as Q goes to zero, $I(Q)$ can be related to the isothermal magnetic susceptibility, which results primarily from electronic excitations.

At short-range distances, both the static *structural* and *magnetic* properties are consistent with the formation of O_4 molecular units in the liquid. To address the stability of such units, we calculated the average residence time following Impey *et al* [16]. For a radius r_c determining neighbouring molecules, the time distribution function is given by

$$n(t) = \sum_{t_n} \sum_{\langle ij \rangle}^{r_{ij} < r_c} P_{ij}(t_n, t), \quad (3)$$

where $P_{ij}(t_n, t)$ takes the value of 1 when the i th and j th molecules remain neighbours between the time steps t_n and $t_n + t$, and of 0 otherwise. The sum over t_n corresponds to a sampling over different time steps in the simulation. The distribution $n(t)$ generally decays exponentially, $n(t) = n(0) \exp(-t/\tau)$, and its damping rate defines the average residence time τ . For $r_c = 3.1 \text{ \AA}$, we found that $n(t)$ is well described up to about $t = 0.6 \text{ ps}$ by a single τ of 0.16 ps (figure 4). Separating the molecular pairs according to their relative geometric orientation, we found average residence times of $\tau_H = 0.20 \text{ ps}$ and $\tau_{\text{other}} = 0.11 \text{ ps}$ for H-type and other types of geometry, respectively. These values fully support the conjecture that the short-range antiferromagnetic correlations result from collisions with appropriate trajectories [4], rather than from the formation of long-living O_4 units. However, the distribution of residence times (histogram in figure 4) also indicates that several long-living molecular O_4 units occur. The residence time of the longest-living O_4 unit ($\tau = 0.8 \text{ ps}$) is found to be comparable with the experimental lifetime in the gaseous phase (1 ps) [17].

4. Conclusions

To investigate the noncollinear magnetism in liquid oxygen, we performed an *ab initio* molecular dynamics simulation in which the electronic and magnetic structures evolve with the

atomic motion. The radial distribution function and the nuclear structure factor were found in good agreement with the respective experimental results. Our simulation shows that parallel geometries dominate for neighbouring molecules. The magnetic structure factor could be derived from the spin density vectors, and shows short-range antiferromagnetic correlations between neighbouring molecules, in good agreement with spin-polarized neutron diffraction experiments. The time evolution in the simulation provides us with a picture in which the large majority of colliding O₂ molecules assume structural and magnetic configurations which closely resemble those in the O₄ molecule. Formation of truly long-living molecular O₄ units also occurs but involves a considerably smaller fraction of O₂ molecules.

Acknowledgments

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