Structural and electronic properties of liquid carbon: \textit{ab initio} molecular-dynamics simulation

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Structural and electronic properties of liquid carbon: 
*ab initio* molecular-dynamics simulation

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**Abstract.** The structural and the electronic properties of liquid carbon have been investigated along the constant-temperature line of 9000 K for the density of 2.9, 5.8, 8.7 and 11.6 g/cm\(^3\) using *ab initio* molecular-dynamics simulations. With increasing density, the average coordination numbers change from 3 to 8 and the bonding states change from covalent bonding to metallic bonding. We have shown that the liquid state is metallic over the wide range of density.

1. Introduction
The structural and the electronic properties of liquid carbon at low pressure were studied for the first time by Galli *et al.*[1] using *ab initio* molecular-dynamics (MD) simulations and it was shown that the liquid carbon is metallic liquid and that the liquid is composed of twofold-, threefold- and fourfold-coordinated atoms. Recently, the melting curve of diamond has been investigated by *ab initio* MD simulations[2, 3]. Johnson *et al.*[4] have investigated the bonding character in liquid carbon near the melting curve by the time-resolved x-ray absorption spectroscopy and shown that, with increasing density, there occurs a change from predominantly *sp*\(^{-}\)-bonded atomic sites to a mixture of *sp*\(^{-}\), *sp*\(^2\)- and *sp*\(^3\)- sites.

In our previous studies\(^5,6\), we have investigated the pressure-induced structural change of liquid carbon using *ab initio* MD simulations. We have shown that the structure of liquid carbon changes drastically with increasing pressure and the structure at extremely high pressure is similar to those of liquid Si and Ge at ambient pressure. This similarity is shown in the shape of the structure factor \(S(k)\), which is characterized by a shoulder on the high-\(k\) side of the first peak of \(S(k)\).

In this paper, we investigate the detailed structural and electronic properties of liquid carbon using *ab initio* MD simulations. We are particularly concerned with the pressure-dependence of the electronic properties of liquid carbon. We calculate the average coordination numbers, the density of states and the electron density distribution of liquid carbon for various thermodynamic conditions.

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2. Method of calculation
To investigate the structural and the electronic properties of liquid carbon, we employ the \textit{ab initio} MD simulation method, which is based on the density functional theory\cite{7, 8}, where the generalized gradient approximation (GGA)\cite{9} is used for the exchange-correlation energy. For the electron-ion interaction we use the ultrasoft pseudopotential\cite{10} for carbon atom.

In the present calculation, the electronic wave functions and the charge density at the $\Gamma$ point are expanded in the plane-wave basis set with the cutoff energy of 20 and 180 ryd., respectively. The Kohn-Sham energy functional is minimized for a given ionic configuration using an iterative scheme based on the preconditioned conjugate-gradient method\cite{11, 12, 13} and the electronic charge density is obtained. Then the force acting on each ion is calculated by the Hellmann-Feynman theorem and the MD simulation is carried out using the force thus obtained to update the ionic configuration at the next time step. The equations of motion are solved using the velocity Verlet algorithm and the temperature of the system is controlled by the velocity scaling method.

In our calculation we consider the liquid carbon systems at four thermodynamic states along the constant-temperature line of 9000 K for the density $\rho = 2.9$, 5.8, 8.7 and 11.6 g/cm$^3$. If we write the density and the volume at $T = 9000$ K and $\rho = 2.9$ g/cm$^3$ as $\rho_0$ and $V_0$, respectively, these four states studied in this paper correspond to the states with $(\rho_0, V_0)$, $(2\rho_0, V_0/2)$, $(3\rho_0, V_0/3)$ and $(4\rho_0, V_0/4)$. The pressure corresponding to these densities are calculated using the expression for the pressure given by Corso and Resta\cite{14}, which is the generalized formula of the reciprocal-space expression for the pressure in the local-density approximation (LDA) originally proposed by Nielsen and Martin\cite{15} to the GGA.

The MD simulation are carried out for the system containing 64 carbon atoms in a cubic supercell. The periodic boundary condition is imposed for three directions. As an initial configuration for the liquid carbon, we first take the diamond structure composed of 64 carbon atoms in the cubic supercell with 2.9 g/cm$^3$ and then melt the system at 9000 K to eliminate the effects of the initial atomic configuration of the diamond structure, and the density is raised up to 5.8, 8.7 and 11.6 g/cm$^3$ for the simulation of the other three thermodynamic states. We chose a time step of 0.97 fs, and carry out the simulation for about 10 - 20 ps. The quantities are obtained by averaging over 5 - 10 ps after the system reached the equilibrium state.

3. Results and discussion
In our MD simulation, the calculated pressures of the systems at 9000 K are 16, 300, 1000 and 2000 GPa for $\rho = 2.9$, 5.8, 8.7 and 11.6 g/cm$^3$, respectively. In figure 1, we show the distribution of the coordination numbers $P(n)$ of the liquid carbon. The $P(n)$ is calculated by counting the number of atoms within a sphere of radius $r_0$ around each atom, where $r_0$ is the position of the first minimum of the radial distribution function $g(r)$. The average coordination numbers (CN) are estimated to be 3.2, 4.4, 5.8 and 7.8 for $\rho = 2.9$, 5.8, 8.7, 11.6 g/cm$^3$, respectively, which are also shown in figure 1. These values of CN are consistent with those obtained by Grumbach and Martin\cite{2}. The change in CN from three to eight with increasing density suggests that the local atomic configuration of the liquid carbon changes significantly. We have shown in our previous studies\cite{5} that the structure of liquid carbon changes drastically from the quantities such as the radial distribution functions and the structure factors.

In figure 2, the density dependence of the electronic density of states (DOS) of liquid carbon is shown. The origin of the energy is taken to be the Fermi level, $E_F$. In the calculation of DOS, we need to take several $k$ points to describe the DOS realistically. We use 8-64 $k$ points in a cubic Brillouin zone and carry out the electronic structure calculation for several configurations obtained by our MD simulations. In the range of density we have investigated, each DOS has finite value at the $E_F$ as shown in figure 2, which shows that the liquid states are metallic states. Galli \textit{et al.}\cite{1} have shown that the liquid carbon at $\rho = 2.0$ g/cm$^3$ is metallic from the DOS and
the electrical conductivity obtained by their \textit{ab initio} MD simulations. The DOS for $\rho = 2.9$ g/cm$^3$ is very similar to that calculated by them\cite{1}. Our result is also consistent with the recent shock-wave experiment\cite{16} at extremely high pressure of 1000 GPa, where it is shown that there occurs the nonmetal-metal transition accompanied with the melting of crystalline diamond.

To investigate detailed electronic properties of liquid carbon, we show in figure 3 the electron density distribution for the density $\rho = (a)2.9$, (b)5.8, (c)8.7 and (d)11.6 g/cm$^3$ at 9000 K. The contour lines on a plane are drawn at intervals of 0.02 a.u. It is seen from figure 3(a) that, at $\rho = 2.9$ g/cm$^3$, the electron density is localized around carbon atoms and there exist covalent-bonding states between carbon atoms. There are $sp^-$, $sp^2$- and $sp^3$- covalent bonds in the liquid at 2.9 g/cm$^3$, and this result is consistent with the distribution of the coordination numbers shown in figure 1. With increasing density, the electron density around carbon atoms becomes denser as shown in figure 3(b), and $sp^3$- bonds increase. At higher density of 8.7 and 11.6 g/cm$^3$, the electron density distributes over the whole system as shown in figures 3(c) and 3(d). These results show that the bonding character changes from $sp^-$, $sp^2$- and $sp^3$- covalent bonding to metallic bonding. From the detailed analysis of the electron density distribution and the distances between carbon atoms, we show that, at 2.9 g/cm$^3$, the covalent bonds between carbon atoms remain for about 0.1-0.2 ps, and then, they start to break and to form a new bond with the other carbon atom. The covalent bonds with finite lifetime in liquid states are also shown for liquid Si by \textit{ab initio} MD simulations\cite{17}.

4. Summary
The structural and the electronic properties of liquid carbon in the wide range of density (pressure) have been investigated using \textit{ab initio} molecular-dynamics simulations. We have shown that when the density is increased from 2.9 g/cm$^3$ to 11.6 g/cm$^3$ at 9000 K, the electron density which is localized around carbon atoms distributes over the whole system, and the
bonding character changes from covalent bonding to metallic bonding. The liquid states are metallic state over the range of density we have studied in this paper. The lifetime of the covalent bonds in liquid carbon at 2.9 g/cm$^3$ are about 0.1-0.2 ps.

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