Structure of liquid metals by *ab initio* molecular-dynamics simulations

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Abstract.   How the study of liquid metals has progressed in the past three decades is summarised briefly from a personal point of view. It is emphasised that, by *ab initio* molecular-dynamics (MD) simulations, we can now obtain the electronic states as well as the structure of liquid metals at the same time and therefore we can understand the characteristic features of the microscopic atomic structure and bonding states *in real space*. As examples we show the results of our *ab initio* MD simulations for liquid phosphorus, liquid tellurium and liquid carbon at high pressures.

1. Introduction

Structure of liquid metals has been studied experimentally and theoretically for a long time. By the classical statistical mechanics, the structure of liquids can be described by the structural functions such as radial distribution function (or pair correlation function) and the structure factor, which are related to the interatomic interactions. In the case of liquid metals, both structure and the interatomic interaction are strongly dependent on electronic states. For these reasons, the structure of liquid metals must be studied based on the classical statistical mechanics and electronic states theory. In the following, I will briefly summarise how the study of liquid metals has progressed in the past three decades from a personal point of view.

2. Structure of liquid metals

In the phase diagram, liquids locate between solid crystals and gases. Though there exist ideal model systems for solid crystals and gases, such as a perfect crystal and an ideal gas, respectively, there is no ideal model system for liquids. From the symmetry of atomic arrangement, solid crystals are periodic systems, while liquids as well as gases are non-periodic system. Liquids near the melting point have similar density to the solid crystal, while the gases have much lower density. There exists short-range order of atomic configuration in liquids, though there is no long-range order. For these reasons, both solid crystals and liquids are classified into a same category, i.e. the *condensed matter*. Liquid metals are two-component systems, which consist of ions and conduction electrons. The atomic (ionic) arrangement, which is time-dependent in the case of liquid, is closely connected with electronic states.Therefore it is important to take into account this connection for describing the structure of liquid metals, which is defined theoretically by the ensemble average of atomic arrangements over space and time and can be obtained by x-ray and neutron diffraction experiments.

Until the middle of 1980s, the structure of liquid was studied by the integral-equation theories (see a review [1]) and computer simulations such as molecular-dynamics (MD) and Monte Carlo (MC) simulations (see e.g. [2]). We need to know the interatomic potential as input information to solve the integral equations and to carry out these simulations. The standard method to obtain the interatomic potential of liquid metals was the pseudopotential perturbation theory [3] at that time. This theory gives rise to the so-called *effective* pairwise interatomic potential, which consists of the direct ion-ion Coulomb interaction and the indirect ion-ion interaction through conduction electrons derived by the second-order perturbation theory. The obtained effective interatomic potential, which consists of attractive as well as repulsive parts, depends on the density of conduction electrons, since the effect of conduction electrons is taken into account by the screening function, which depends on the density of conduction electrons. Though the pseudopotential perturbation theory was successfully applied to simple liquid metals such as liquid alkali metals, there are some limitaions of its validity;

e.g. the electron-ion pseudopotential must be weak, though it is not always the case. More seriously, it is difficult to take account accurately of the many-body interaction beyond the pairwise interaction, which depend on both ionic arrangement and electronic states.

An epoc-making breakthrough in the study of liquid metals was the new method proposed by Car and Parrinello [4] in 1985, which is a unified method of the molecular-dynamics simulation for ionic dynamics and of the density-functional theory (DFT) for electronic states, and enables us to obtain simultaneously both ionic arrangement and electronic states at the same time. The electronic wavefunctions as well as the ionic coordinates are dynamical variables in this method and are treated by Lagrange equations of motion. The most important feature of this new method is that the interatomic potential need not to be given as input information, since the force acting on each atom is given within the framework of this method, i.e. the force can be calculated from the DFT energy functional by the Hellmann-Feynman theorem. This new method is now called *ab initio* molecular-dynaics simulation method, since no empirical parameters are included. The density functional theory was originally proposed by Hohenberg and Kohn [5] and Kohn and Sham [6] in the middle of 1960s and had been extensively used for the electronic band structure calculation of periodic systems in solid state physics and for the electronic states of atoms and molecules in quantum chemistry. The newly proposed Car-Parrinello method extended the applicability of the density functional theory to non-periodic systems such as liquid metals and semiconductors, various surface systems, nanomaterials and so on.

Since the proposal by Car and Parrinello, different schemes of *ab initio* MD simulation methods have been proposed [7, 8, 9] , in which DFT energy functional is minimised for each ionic configuration using some optimisation method. Therefore, this method is called 'the dynamics on the Born-Oppenheimer surface', since the electronic states are always ground states at each MD step, i.e. for each ionic configuration. We employ this scheme of the *ab initio* MD simulation method, which is based on the density functional theory, where the generalised gradient approximation (GGA) [10] and the local-density approximation (LDA) [11, 12] are used for the exchange-correlation energy. For the electron-ion interaction we use the ultrasoft pseudopotentials [13] and the norm-conserving pseudopotentials [14]. The electronic wavefunction is expanded in the plane-wave basis set and the Γ point is used for Brillouin zone sampling. The Kohn-Sham energy functional is minimised for a given ionic configuration using an iterative scheme based on the preconditioned conjugate-gradient method and the electron 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 Newton's equations of motion are solved using the velocity Verlet algorithm and the temperature of the system is controlled by the Nosé-Hoover thermostat technique [15, 16].

In the past two decades since 1985, the structure of liquid metals has been studied by many people using various schemes of *ab initio* MD simulations. In this paper I do

not intend to review these studies but emphasise the importance of the real-space point of view.

3. Application of *ab initio* MD simulations to various liquids

In 1980 Heine and his collaborators published a review book [17] , in which Heine proposed that *throwing out k-space* is important to discuss the electronic properties of non-periodic systems such as surface systems and amorphous materials. Heine and others developed a real-space method, so-called recursion method based on Green's function formalism. Traditionally, the solid state physics has been based on k-space formalism such as energy band structure calculations, and the quantum chemistry has been based on real-space formalism such as molecular-orbital theory. Such a real-space approach is now possible in the structural study of liquid metals, which are structurally disordered systems, using *ab initio* MD simulations. In this connection, it should be noted that Chelikowsky *et al* [18] proposed a real-space finite-difference method for solving Kohn-Sham equation and that the real-space method has been applied to various systems, e.g. to nanostructures [19] and liquid metals [20].

It is well known that the liquid silicon is metallic, though the solid silicon is a typical semiconductor with tetrahedral covalent bonds. Štich *et al* [21] investigated how the liquid silicon becomes metallic using *ab initio* MD simulation, and showed that the covalent bonds break when the distance of two adjacent atoms exceeds a critical bond length of about 2.5 Å, since atoms in the liquid state move around due to temperature effects, which suggests that there remain some covalent bonds with finite lifetime in the liquid silicon. In this way, they showed the change of bonding character due to atomic dynamics in real sapce. The metallic nature of the liquid silicon was also confirmed from the calculated electronic density of states, which has finite values at the Fermi level.

In this section we show some examples for the structure of liquids, the characteristic features of which can be studied only using the *ab initio* MD simulation method, in the sense that the structural changes of these liquids are closely related to the changes in the electronic states of those liquids.

3.1. Pressure-induced structural phase transition in liquid phosphorus

Katayama *et al* [22] showed by x-ray diffraction experiments that there occurs a pressure-induced liquid-liquid phase transition in liquid phosphorus at 1 GPa, which was considered to be a pressure-induced first-order structural phase transition from the molecular liquid to the polymeric liquid. It was confirmed by *ab initio* MD simulations for liquid phosphorus [23, 24] that the structural transition corresponds to the transition from the lower-density molecular liquids composed of stable tetrahedral P_4 molecules to the higher-density polymeric liquid with complex network structure as is shown in figure 1. The P_4 molecule is formed by four covalent bonds, which can be understood from the calculated electronic charge density shown also in figure 1. Furthermore we [23] showed

from our calculated electronic density of states shown in figure 2 that this pressure-induced structural transition corresponds to the nonmetal-metal transition from the nonmetallic molecular liquid composed of stable P_4 molecules to the metallic polymeric liquid.

(a)   (b)
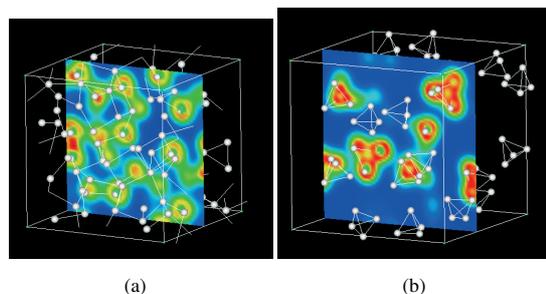
Figure 1. The snapshots of ionic configurations and the electron density distribution for liquid phosphorus with (a)the higher density $\rho=2.8$ g cm^{-3} and (b)the lower density $\rho=1.7$ g cm^{-3}. Phosphorus ions are shown by white balls and the P-P bonds are drawn for P ion pairs within the cut-off distance of 2.6 Å. The contour curves show the electron density distributions on the plane [23].

This is a good example for the change in the electronic states accompanied with the structural change, which can be clarified by the *ab initio* MD simulation.

We [25] have also shown by the *ab initio* MD simulation that there exist stable 'Zintl ions' $(Pb_4)^{4-}$ in the compound-forming liquid $K_{0.8}Pb_{0.2}$ alloy and that the observed structure factor characterised by the first sharp diffraction peak can be reproduced, which arises from the intermediate-range ordering of Zintl ions. Such a chemical short-range order in compound-forming liquid alloys can now be studied by *ab initio* MD simulations.

3.2. Change of bonding character in liquid tellurium under pressure

Since the wavefunction is expanded in the plane waves in the standard *ab initio* MD method, it spreads over the whole system and therefore it is not suitable to investigate the local property such as bonding characters. For this purpose, as pointed out by Heine, it is helpful for understanding the bonding character to use the concepts of quantum chemistry, such as the Mulliken population analysis [26]. In the case of *ab initio* MD simulation, we can discuss the bonding properties between neighbouring atoms using *the bond overlap population*, which can be obtained by projecting the DFT wavefunction to the atomic orbitals and calculating the overlap integrals. The bond overlap population
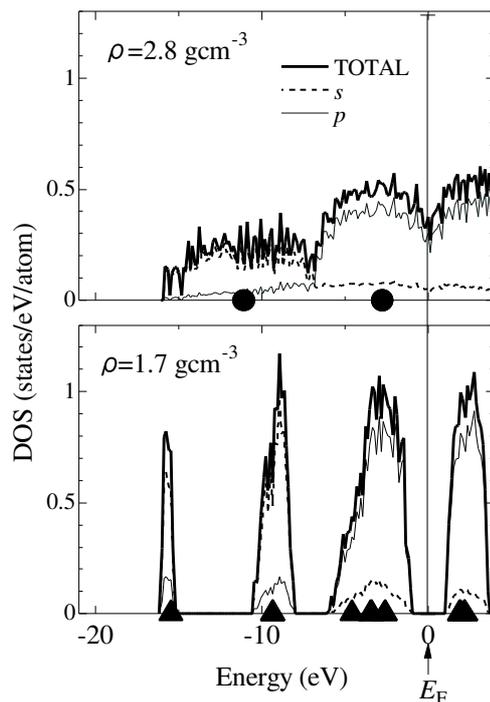
Figure 2. The total and the angular-momentum-decomposed (partial) density of states (DOS) for the higher-density ρ=2.8 g cm^{-3} (upper panel) and the lower-density ρ=1.7 g cm^{-3}(lower panel) liquid phosphorus. The total DOS is calculated by sampling 10 k-points of the Brillouin zone and by averaging over some ionic configurations. The partial DOS's are obtained by projecting the wavefunctions on the spherical harmonics within a sphere of R_c centred at each atom, where R_c is chosen to be about half of the average nearest-neighbour distance. The energy levels of a P atom and a tetrahedral P$_4$ molecule in the gas phase are indicated by the solid circles and the solid triangles, respectively [23].

was originally introduced in the quantum chemistry to measure the strength of covalent bonds in molecules from the real-space point of view.

We [27] studied the pressure dependence of the structural and electronic properties of liquid tellurium using *ab initio* MD simulations to clarify the reason for the experimentally observed anomalous structural change [28], in which, with increasing pressure, nearest-neighbour distance increases first and then decreases and therefore the compression is not uniform. Our analyses including the bond overlap population clarified that there are two stages in the compression of the liquid tellurium. In the first stage up to 6 GPa, we showed that the elongation of the nearest-neighbour distance is due to weakening of covalent bonds, while in the second stage, the anisotropy of the atomic configuration around each tellurium atom is reduced due to the compression of increasing pressure.
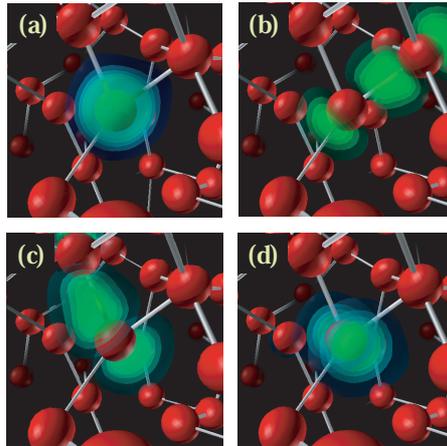
Figure 3. Spatial distribution of maximally localised Wannier functions in liquid tellurium at ambient pressure. The red balls show the positions of Te atoms. Two Te atoms, whose distance apart is shorter than 3.3 Å, are connected by a bond [30].

In order to investigate the bonding character in real space, Morzari and Vanderbilt [29] proposed a practical method to generate maximally localised Wannier functions (MLWF). We [30] also demonstrated that MLWFs are highly useful for investigating the electronic properties of the liquids consisting of covalently bonded atoms. We have shown how bonding character of liquid tellurium changes with increasing pressure. As an example we show in figure 3 the spatial distribution of MLWFs in liquid tellurium at ambient pressure. Figure 3(a) shows that the 5s electrons of Te form a spherically distributed MLWF around a Te atom. Figures 3(b) and 3(c) show two σ-type bonding states around the Te atom and the lone pair state is shown in figure 3(d). These results show that we can obtain the spatial distribution of the bonding states in the liquid Te. The change in the bonding character due to pressure was discussed in detail in [30].

We can now understand the bonding character of liquid metals and semiconductors based on the real-space quantities such as bond overlap population and the maximally localised Wannier functions.

3.3. Structure of liquid carbon under extremely high pressures

Since there are sp-, sp^2- and sp^3-bonding states for carbon, there exist various structures such as diamond, graphite, fulleren, carbon nanotube and graphene. Galli *et al* [31] studied for the first time the structural and electronic properties of liquid carbon at low pressure by *ab initio* MD simulation and showed that the liquid carbon is metallic.

We [32, 33] have studied the pressure-induced structural change of liquid carbon for a wide range of pressure from 16 GPa to 2000 GPa at 9000 K using *ab initio* MD simulation. Though there are many empirical interaction potentials such as Brenner potential [34] and the environment-dependent interaction potential (EDIP) [35] are proposed for carbon, they are not applicable to the carbon systems for a wide range of pressures or densities, since the bonding character changes drastically from covalent sp-, sp^2- and sp^3-bondings to metallic bonding at extremely high pressures. Even in such a case, however, *ab initio* MD simulation can be applicable due to the transferability of pseudopotentials.

We have shown that the structure factor of liquid carbon changes its shape qualitatively at extremely high pressure and becomes similar to those of liquid silicon and germanium at ambient pressure, which is characterised by a shoulder on the high-wavenumber side of the first peak of the structure factor. In figure 4 we show the density or pressure dependence of the structure factor of liquid carbon obtained by our *ab initio* MD simulation. In our simulation, we took 64 carbon atoms in a cubic supercell and the periodic boundary conditions were imposed. The simulation was carried out for 10 - 20 ps with a time step of 0.97 fs. Furthermore we have shown from the average coordination number, the bond-angle distribution, the electron density distribution and the bond overlap population that the bonding character changes from covalent-bonding to metallic-bonding with increasing pressure. Figure 5 shows the density dependence of the electron density distribution of liquid carbon obtained by our *ab initio* MD simulation and we can see, in real space, that the bonding character changes with increasing density.

The pressure-temperature phase diagram of carbon is known experimentally only in the low pressure region, though there exists a theoretically predicted phase diagram [36, 37]. Our calculation supports the predicted phase diagram in the sense that our results are consistent with the phase diagram, in particular, the existence of the maximum of melting temperature of diamond is predicted.

The most important missions of computer simulations are to predict the properties of systems, which are difficult to study experimentally, and to suggest guiding principle for future experimental plan.

4. Summary and future problems

As mentioned above, the proposal of *ab initio* MD method in 1985 was an epock-making event and applications of the new method in the past two decades have been contributing
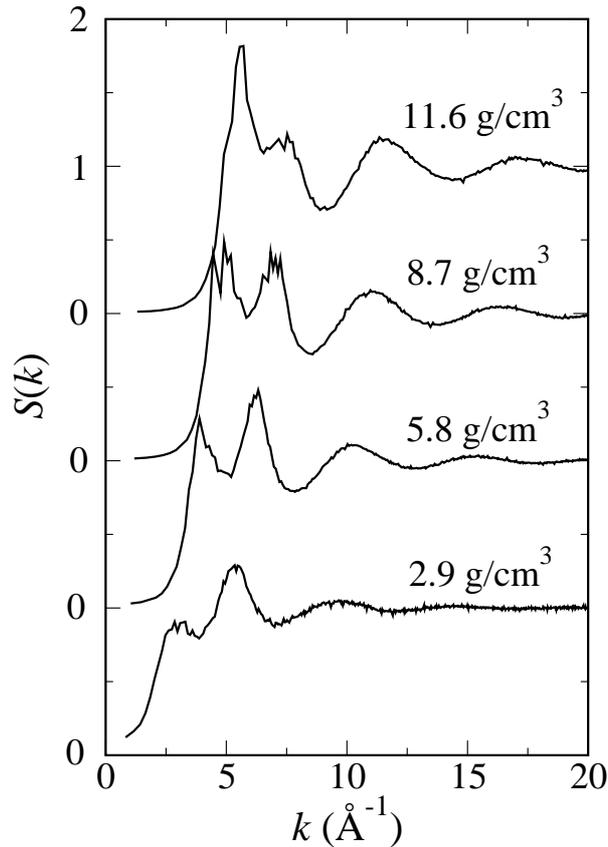
Figure 4. The structure factor of liquid carbon calculated by our *ab initio* MD simulations for ρ=2.9, 5.8, 8.7 and 11.6 g cm^{-3} at 9000 K [32].

substantially to the progress in understanding the structural and electronic properties of liquid metals from a real space point of view.

Finally I would like to mention some future problems related to *ab initio* MD simulations. Needless to say, any research is endless, and *ab initio* MD simulation method itself is not complete and still developping for the following reasons.

- The methodological problems have not been completely solved. The most serious problem in the DFT is the accurate treatment of the electron correlation energy, which is a too difficult many-body effect to treat exactly. Various approximations such as the GW approximation have been proposed to apply the DFT to strongly correlated systems [38].

- Relatively small systems have been studied so farcomparing with the classical MD simulations, since *ab initio* MD simulation needs a large amount of computer resorces. Recently, however,various order-N methods and hybrid methods have been proposed and applied to large scale systems [38].

- The improvement of the algorithm such as a pararellisation technique is in progress ([20] and references therein).The power up of computer's ability is still progressing
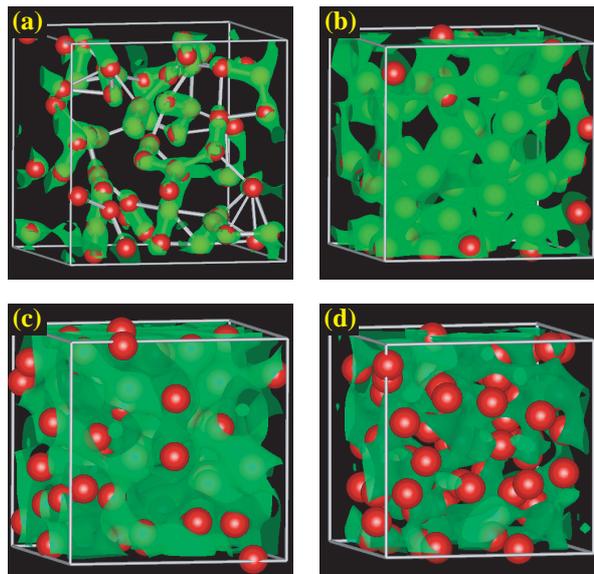
Figure 5. The electron density distribution of liquid carbon calculatede by our *ab initio* MD simulations for ρ=(a)2.9, (b)5.8, (c)8.7 and (d)11.6 g cm^{-3} at 9000 K. The green surfaces show the surfaces with the constant electron density of 0.25 a.u.[32].

and promising, though our demand is endless.

- The *ab initio* MD method is not almighty. There exist some problems [39] with large length scale and/or with long time scale beyond those scales which can be treated by *ab initio* MD methods at present. We need to develop a new method such as multi-scale simulation methods to treat such problems.

Acknowledgments

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