

Dynamic properties of liquid germanium studied by an *ab initio* molecular-dynamics simulation

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Abstract Dynamic structures of liquid germanium at the temperature of 1253 K were investigated by a long-time (66 ps) first-principles molecular-dynamics simulation. The calculated structure factor is in good agreement with the results of the neutron and x-ray diffraction experiments. It is found that an atom diffuses quickly not only when its coordination number becomes smaller but also when surrounding atoms are moving together to almost the same direction. Moreover we found out that each atom migrates staying in a group of several neighboring atoms for 0.3 ~ 0.5 ps. The calculated dynamic structure factors and the dispersion relation are in excellent agreement with the result of the recent x-ray inelastic scattering experiment.

1 Introduction

The structure of liquid germanium is complicated compared with most liquid metals. Unlike simple liquids, the structure factor $S(Q)$ has a shoulder on the high- Q side of the main peak [1, 2]. This shoulder is explained by the difference between the effective core radius and the wavelength of the Friedel oscillation in the interatomic pair potential [3] or the existence of the covalent bonds even in the liquid metal [4].

It is an interesting issue that how such complex structures are related to the dynamic structure in the liquid germanium. One of the fundamental physical properties on the dynamics is the diffusion phenomena. Unfortunately it is not easy to measure the accurate diffusion coefficient of liquid metals on the earth because of the existence of the convection. In our project we have a plan to carry out the experiments for the diffusion coefficients in liquid silicon, germanium and their alloys using a microgravity environment at the International Space Station. On the theoretical side, an *ab initio* molecular-dynamics (AIMD) simulation is one of the best methods for studying the liquid germanium which is a metal but may have covalent bonds. Though several AIMD simulations for liquid germanium [5, 6] have been carried out so far, dynamic properties have not been studied so much.

Recently the dynamic structure factor $S(Q, \omega)$ of liquid germanium was measured by the x-ray inelastic scattering experiment [7]. The dynamic structure factor is an important quantity to understand the collective motion and also the relation between the structure and the diffusion properties. In the present study we performed an AIMD simulation for liquid germanium at 1253 K and calculated $S(Q, \omega)$. A particular emphasis in this study is placed on an extremely long time, 66 ps, simulation, which gives an excellent statistical

accuracy for the dynamic properties. The purpose of this paper is to clarify the relation between a single-atomic motion and local structures in liquid germanium at 1253 K.

2 Method of calculation

Our method of calculation is based on the density functional theory with the generalized gradient approximation (GGA) [8] for the exchange-correlation energy. The norm-conserving pseudopotential [5] is employed for the interaction between valence electrons and the ion, which is derived from the calculation of the atomic electron configuration $4s^2 4p^2 4d^0$. The electronic wavefunctions are expanded by a plane wave basis set with the cutoff energy of 11 Ryd. The Γ -point is only used to sample the Brillouin zone of the MD supercell. The Kohn-Sham energy functional is minimized by the preconditioned conjugate-gradient method [5, 9]. The constant temperature AIMD simulation is carried out using 64 atoms in a cubic supercell with periodic boundary conditions. The Nosé-Hoover thermostat is used for the temperature control. The density of the system is chosen from the experimentally observed value; the number density $n = 0.04658 \text{ \AA}^{-3}$ [10]. To calculate the dynamic structure factor accurately, we performed a long-time MD simulation for 22 000 steps with a time step of 125 a.u. (3.02 fs).

3 Results and Discussions

3.1 Static structure

In Fig. 1, we show the structure factor $S(Q)$ of liquid germanium at 1253 K. The solid line represents the result calculated from the AIMD. The data observed from the x-ray [1] and the neutron [2] diffraction experiments are also shown by the open and the solid circles, respectively. The asymmetric first peak of the experimental $S(Q)$ is well reproduced by the AIMD simulation and the whole shape of $S(Q)$ is in good agreement with the experimental data.

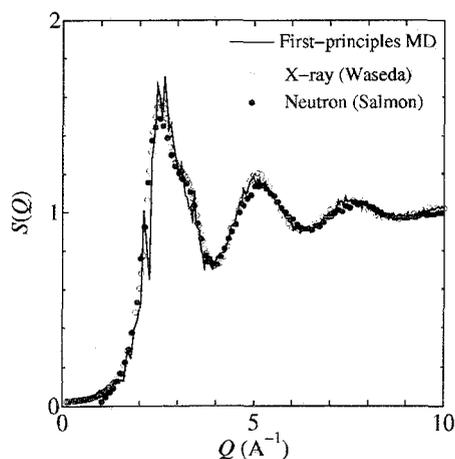


Figure 1. Structure factors of liquid germanium at 1253 K. The solid line, the solid and the open circles show the results calculated by the AIMD, the x-ray [1] and the neutron scattering experiments [2], respectively.

3.2 Dynamic structure

To investigate the single-atomic motion in liquid germanium, we calculate the mean square displacement of atoms (MSD) and the velocity autocorrelation function (VAF) by averaging over all 64 atoms and over time origins in the whole MD steps. The MSD shows the free-particle like behavior until about 0.1 ps and the following straight line in a long-time region with excellent statistical accuracy (see Fig. 3 (a)). The VAF does not take large negative values. This implies that the *cage effect* is small in liquid germanium. The self-diffusion coefficient D estimated from the MSD and from the spectrum of the VAF are 0.89×10^{-4} and 0.90×10^{-4} cm²/s, respectively. These results are in good agreement with the experiment [11].

Since the value of D may be sensitive to the density of the system in the AIMD simulation, we also used the smaller density of $n = 0.04526$ Å⁻³ [12], which is 3 % smaller than the previous density, and examined the density dependence of the structure by performing AIMD simulation for 10 000 steps. In this case the size of the MD supercell is $L = 11.22$ Å and the result of the self-diffusion coefficient D is 0.98×10^{-4} cm²/s, which is 10 % larger than that for the system of the higher density.

In Fig. 2 the dynamic structure factors $S(Q, \omega)$'s for five Q values are shown. The solid lines show the results calculated from the AIMD. The experimental results [7] are also presented by the open circles (raw data) and the dashed lines (fitting curve) in Fig. 2. The side peak for $Q = 0.6$ Å⁻¹, which shows a longitudinal propagating mode, is well reproduced by the AIMD simulation. With increasing the wavenumber Q , the side peak becomes to be less recognized. The central peak in $S(Q, \omega)$ becomes sharper and higher around $Q = 2.5$ Å⁻¹ which is the main peak position of $S(Q)$, that is called de Gennes narrowing. The dispersion relation, which is the relation between Q and the frequency ω_p , was also calculated, where $\omega^2 S(Q, \omega)$ is maximum. The gradient of the dispersion relation in a small Q -region agrees reasonably with the experimental sound velocity 2682 m/s [13]. In summary the calculated $S(Q, \omega)$ is in excellent agreement with the experiment and this fact proves the accuracy of the dynamic properties in our simulation.

To clarify the relation between the single-atomic motion and the local structure in more detail, we show the following dynamic properties for one atom (tagged with the number 1) in Fig. 3: First, we note the time dependence of the square displacement of the atom (thick solid line) and its coordination number n_c (histogram) for a period of 2 ps from a time of origin. The MSD is also shown by the dashed line. Here the coordination number n_c is defined as the number of the other atoms within the cutoff radius $r_c = 2.7$ Å, which is the average nearest neighbor distance. In this definition, the average coordination number is 2.1. Second, we note the time dependence of the force on the atom 1 $\vec{F}_1(t)$. The three lines represent the x, y and z elements of the force, respectively. Note that not only the neighboring atoms but also all atoms in the system contribute the force. Third, we note the velocity correlation between the velocity of atom 1 $\vec{v}_1(t)$ and that for its neighbor atoms, which is calculated by the inner product of $\vec{v}_1(t)$ and the average velocity of the coordinating atoms $\vec{v}_{1c}(t)$. Fourth, we note the tag number of the neighboring atoms within $r_c = 2.7$ Å from the atom 1.

From now on we discuss the single-atomic motion based on above dynamic properties. We can roughly divide this period of 2 ps into the four stages from a point of view of the

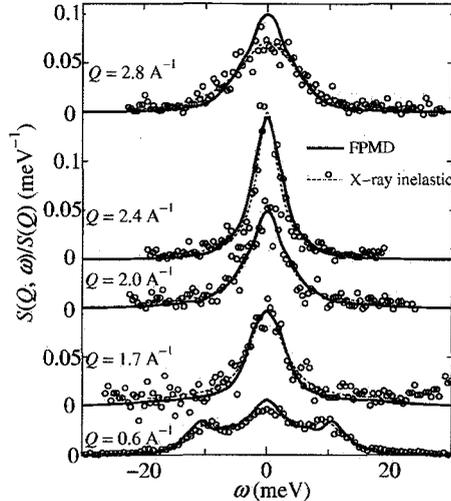


Figure 2. The dynamic structure factors $S(Q, \omega)$'s of liquid germanium at 1253 K. The solid lines show the calculated results by the AIMD simulation. The circles represent the raw experimental data and the dashed lines are the fitting curves of the damped harmonic oscillator model [7].

member of the neighbor atoms in Fig. 3 (d): first stage ($0.1 < t < 0.6$ ps), second stage ($0.7 < t < 1.2$ ps), third stage ($1.3 < t < 1.7$ ps) and final stage ($t > 1.8$ ps).

It is found from Fig. 3 (a) that an atom diffuses largely when its coordination number is small, $n_c = 0 \sim 2$, for example, at times of $0.5 < t < 0.6$ ps and $1.2 < t < 1.35$ ps which correspond to the periods when one stage transitions to the next stage. In these periods of time, since the force on the atom 1 is small, the atom can diffuse freely.

On the other hand, for $0.25 < t < 0.5$ ps in the first stage, though the coordination number is not small, $n_c = 2 \sim 3$, the displacement of the atom is large. In this period, the velocity correlation $\vec{v}_1(t) \cdot \vec{v}_{1c}(t)$ almost always takes large and positive values. In addition to this, from the Fig. 3 (d), we can see the four atoms are involved in the first stage; though the atom 1 diffuses over 2 \AA during this 0.5 ps, the member of the coordinating atoms is unchanged. These features imply that the atom 1 is connected with its neighbor atoms and moves together almost the same direction with keeping the unit of atoms.

At $0.8 < t < 1.2$ ps in the second stage, the atom 1 is staying at almost the same position. In this period, the atom is affected by the larger and oscillating forces from the all directions. Besides this, the velocity correlation $\vec{v}_1(t) \cdot \vec{v}_{1c}(t)$ is almost zero. These structural properties imply that the atom 1 is trapped by its neighbor atoms and makes a group of the atoms. It is known that the effective packing fraction of liquid germanium is small and hence the *cage effect* is also small: In fact as mentioned above the VAF does not show the distinct *cage effect*. Nonetheless we found out there exist structures of atoms which play a role of a cage for a time of ~ 0.5 ps.

After $t \sim 1.2$ ps, the atom 1 migrates to the next group of the atoms, which consists of the same three atoms as before and other two new atoms. We can see from Figs. 3 (a) and (d) that, the atom 1 stays in this new group of atoms for about 0.3 ps and escapes from it at $t \sim 1.75$ ps. The next members of the four neighboring atoms are all new. That

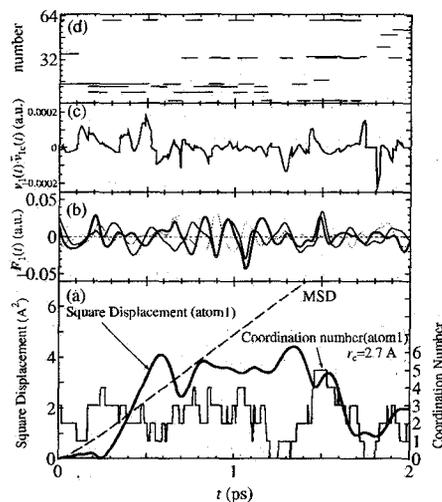


Figure 3. (a) The time dependence of the square displacement of the atom 1 (line) and its coordination number (histogram). The MSD is also shown by the dashed line. (b) The force on the atom 1 $\vec{F}_1(t)$. The three lines show the x , y and z elements of $\vec{F}_1(t)$, respectively. (c) The velocity correlation $\vec{v}_1(t) \cdot \vec{v}_{1c}(t)$ between the velocity of the atom 1 $\vec{v}_1(t)$ and the average velocity of coordinating atoms $\vec{v}_{1c}(t)$. (d) The tag numbers of the coordinating atoms around the atom 1.

is to say it takes over 1 ps for an atom to escape from its neighboring atoms.

The snapshot of atomic configurations and the electronic density distributions of liquid germanium at 0.42 and 1.06 ps are shown in figure 4. The atom 1 is shown by the red ball and its neighbor atoms are shown by the white balls. When the distance between any two atoms is less than 2.5 Å, a bond is drawn. The left two figures show the total charge density distributions. The red and blue colors mean areas of higher and lower electronic density, respectively. To obtain information of chemical bonds in the liquid system, the excess charge density distributions are also shown in the right four figures. The areas of red and blue mean the positive and negative values of the excess charge density. The positive values of the excess charge density implies that a certain chemical bond is formed in a short time in liquid germanium.

4 Conclusions

To clarify the relation between the single-atomic motion and the local structure in liquid germanium at 1253 K, we carried out the AIMD simulation for 66 ps. We have found out the following three types of the diffusion processes: (i) An atom moves freely when its coordination number becomes smaller: That is a time, for example, when the members of the coordinating atoms are changing. (ii) An atom moves together with forming a group with its neighbor atoms. (iii) An atom stays almost the same position when it is trapped by a group of neighboring atoms. It is also found that each atom stays in a group of the neighboring atoms for 0.3 ~ 0.5 ps. The analysis of the diffusion properties in terms of the dynamic structure factor $S(Q, \omega)$ is now in progress.

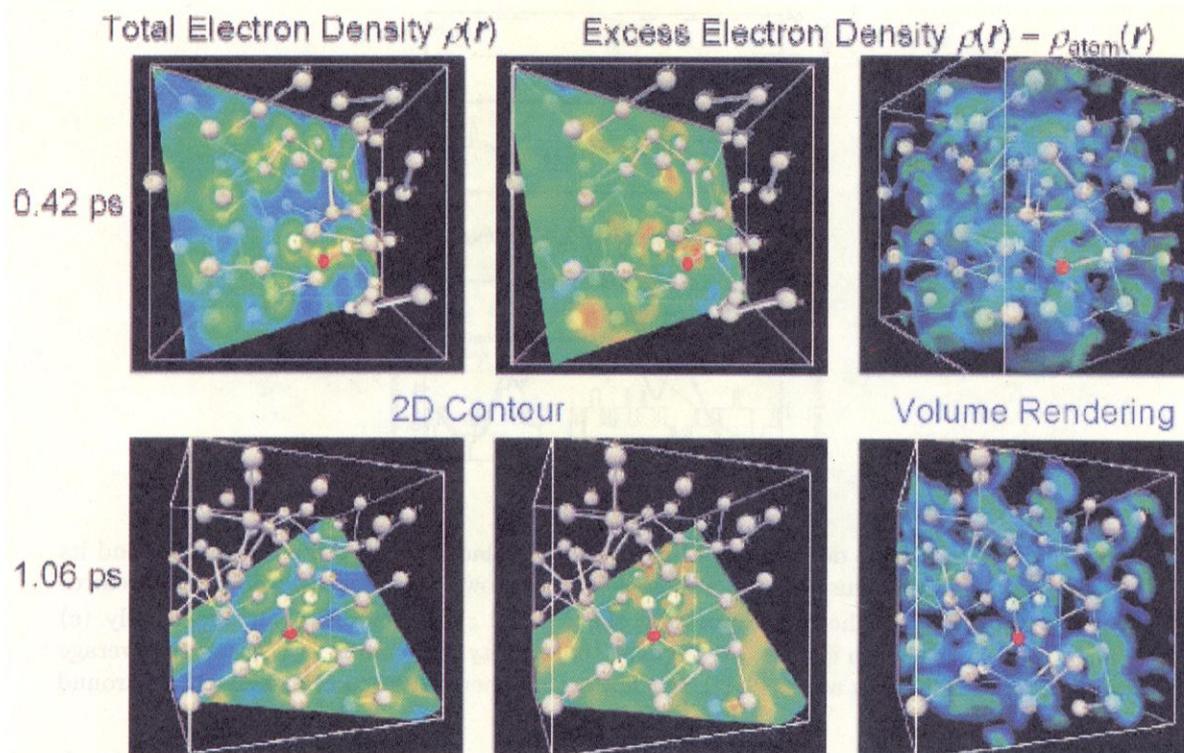


Figure 4. The snapshot of atomic configuration and the electronic charge density distribution.

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