Dynamic structure of liquid germanium by a first-principles molecular-dynamics simulation

S. Munejiri, F. Shimojo†, K. Hoshino† and T. Itami‡

NASDA, Tsukuba 305-8505, Japan
† Hiroshima University, Higashi-Hiroshima 739-8521, Japan
‡ Division of Chemistry, Graduate School of Science, Hokkaido Univ., Sapporo 060-0810, Japan

Abstract Dynamic structures of liquid germanium at the temperature of 1253 K were investigated by a first-principles molecular-dynamics simulation. To investigate long-range correlation functions the MD simulation was carried out not only with a cubic cell but also with a rectangular parallelepiped cell. The calculated dynamic structure factors and the dispersion relation are in excellent agreement with the results of a recent inelastic X-ray scattering experiment.

1 Introduction

The structure of liquid germanium is complicated compared with that of 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. Recently the dynamic structure factor, $S(Q,\omega)$, of liquid germanium was measured by the inelastic X-ray scattering experiment [5].

On the theoretical side, a first-principles molecular-dynamics (FPMD) simulation is one of the best methods for studying the properties of liquid germanium. Though several FPMD simulations for liquid germanium [6, 7] have been carried out so far, dynamic properties have not been much studied in detail.

In this paper we present the results of the dynamic properties of liquid germanium at 1253 K calculated by FPMD simulations. The system size dependence of the self-diffusion coefficient is also investigated.

2 Method of calculation

2.1 *First-Principles MD*

Our first-principles calculation is based on the density functional theory with the generalized gradient approximation (GGA) [8] for the exchange-correlation energy. The norm-conserving pseudopotential [6] is employed for the interaction between the 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 a cutoff energy of 11 Ryd. The Γ-point is only used to sample the Brillouin zone of the MD supercell. The Khon-Sham energy functional is minimized by the preconditioned conjugate-gradient method [6, 9]. The constant temperature FPMD simulation is carried out using the Nosé-Hoover [10, 11] thermostat. The density of the system is chosen from the experimentally observed value; the number density $n = 0.04658$ Å^{-3} [12].

2.2 *MD simulation*

We carried out the FPMD simulation using 64 atoms in a cubic cell with periodic boundary conditions (system 1). The length of a side of the cell, L, is 11.12 Å. 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). Physical properties were calculated by averaging the atomic configurations of 21,500 steps after the thermodynamic equilibrium was achieved.

In the system 1, the smallest wavenumber, Q_{min}, is $2\pi/L = 0.57$ Å^{-1} . On the other hand, experimental dynamic structure factors were observed for $0.2 < Q < 2.8$ Å^{-1} [5]. To obtain the dynamic structure factors for smaller-Q region we employ a larger system with 128 atoms (system 2). The shape of the MD cell in the system 2 is not cubic but a rectangular parallelepiped whose one side length L_1 is as twice as those of the other sides, L_2 and L_3, where $L_1 = 22.23$ and $L_2 = L_3 = 11.12$ Å. In this system the smallest wavenumber, Q_{min}, is $2\pi/L_1 = 0.28$ Å^{-1} . For the system 2 the MD simulation was carried out for 25,000 steps with a time step of 3.02 fs.

2.3 *Dynamic structure*

The method of calculation of the dynamic structure factor $S(Q,\omega)$ is as follows: First we calculate the intermediate scattering function $F(Q,t)$ which is defined as the space Fourier transform of the van Hove correlation function $G(r,t)$,

$$\begin{aligned} F(Q,t) &= \int d\boldsymbol{r} \exp(-i\boldsymbol{Q}\cdot\boldsymbol{r})G(r,t) && (1) \\ &= \frac{1}{N}\left\langle n_{\boldsymbol{Q}}(t)n_{-\boldsymbol{Q}}(0)\right\rangle, && (2) \end{aligned}$$

where

$$n_{\boldsymbol{Q}}(t) = \sum_{j=1}^{N} \exp(i\boldsymbol{Q}\cdot\boldsymbol{r}_j(t)) \tag{3}$$

is the Fourier transform of the density operator, $\langle\cdots\rangle$ means thermal average and N is the number of atoms. The dynamic structure factor $S(Q,\omega)$ is given as

$$S(Q,\omega) = \int dt \exp(-i\omega t)F(Q,t). \tag{4}$$

$S(Q,\omega)$ gives the frequency spectrum of the correlation between density fluctuations of a given wave vector. We note that

$$\frac{1}{2\pi}\int d\omega S(Q,\omega) = F(Q,0) = S(Q) \tag{5}$$

is the static structure factor. The self-diffusion coefficient D is obtained by the relation,

$$D = \frac{1}{6t}\left\langle r^2(t)\right\rangle, \tag{6}$$

where $\langle r^2(t) \rangle$ is the mean square displacement(MSD) of atoms. This expression for D, which is a time-independent quantity, should be applied to the time region where $\langle r^2(t) \rangle$ varies linearly with t. In a fluid system the linear behavior in $\langle r^2(t) \rangle$ is obtained at much longer time compared with the characteristic time of correlation between the tagged atom and its immediate neighbors. Therefore equation (6) is valid only for a large t. The velocity autocorrelation function $Z(t)$ is defined by

$$Z(t) = \frac{1}{N} \sum_{j=1}^{N} < \boldsymbol{v}_j(t) \cdot \boldsymbol{v}_j(0) >, \tag{7}$$

where $\boldsymbol{v}_j(t)$ is the velocity of the j-th atom at time t.

3 Results and Discussion

3.1 *Static structure*

In figure 1, we show the structure factors $S(Q)$'s of liquid germanium at 1253 K. The solid and the dashed lines represent the results calculated by the systems 1 and 2, respectively. 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 $S(Q)$ is well reproduced by the FPMD simulation and the whole shape of $S(Q)$ is in good agreement with the experimental data.

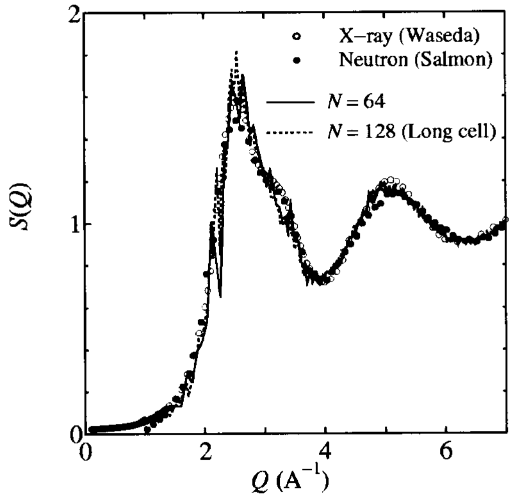

Figure 1. Structure factor, $S(Q)$, of liquid germanium at 1253 K. The solid and the dashed lines show the results for the system of 64 atoms and 128 atoms, respectively. The open and the solid circles show the X-ray [1] and the neutron scattering experiments [2], respectively.

The radial distribution functions $g(r)$'s of liquid germanium at 1253 K are shown in figure 2. The meaning of lines is same as that in figure 1. The first peak for the system 2 is a little broader than that for the system 1.

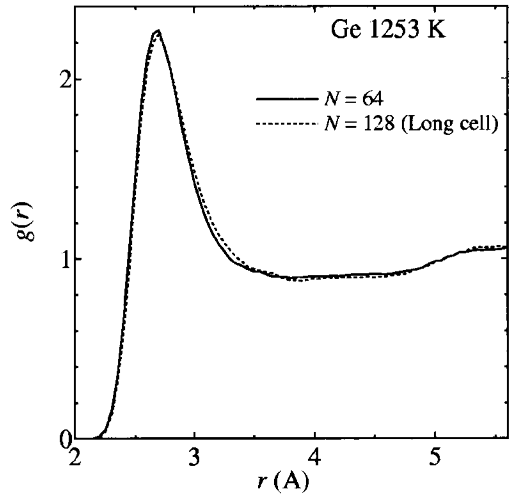

Figure 2. Radial distribution function, $g(r)$, of liquid germanium at 1253 K. The solid and the dashed lines show the results for the system of 64 atoms and 128 atoms, respectively.

3.2 *Three-body angle distribution function*

A three-body angle distribution function $g^{(3)}(\theta, r_c)$ is calculated and shown in figure 3. The three-body angle θ is formed by a pair of vectors drawn from a reference atom to any other two atoms within a cutoff radius r_c. When the cutoff radius r_c is 3.0 Å, which is longer than the average nearest neighbor distance, 2.7 Å, $g^{(3)}(\theta, r_c)$ shows a clear peak centered at 60°. When an interatomic interaction is isotropic and the atoms are in closed-packed, $g^{(3)}(\theta, r_c)$ should have a peak around 60°. Therefore this peak indicates a typical structure in a simple liquid. With decreasing the cutoff radius r_c, the peak at 60° disappears. For $r_c = 2.7$ Å, $g^{(3)}(\theta, r_c)$ shows only single broad peak near 100° which is close to the tetrahedral bond angle of 109°. This peak suggests that some local structures due to anisotropic interactions remain in liquid germanium. The peak around 100° for the system 2 is lower than that for the system 1.

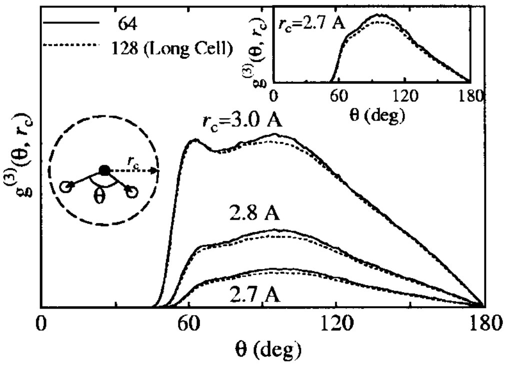

Figure 3. Three-body angle distribution function $g^{(3)}(\theta, r_c)$ of liquid germanium at 1253 K. The solid and the dashed lines show the results for the system of 64 atoms and 128 atoms, respectively.

3.3 *Dynamic structure*

To investigate the single-atomic motion in liquid germanium, we calculated the mean square displacement of atoms (MSD) and the velocity autocorrelation function (VAF) by averaging over all atoms and over the time origins in the whole MD steps. The results of the MSD and the VAF are shown in figures 4 and 5, respectively. The solid and dashed lines show the results obtained by the systems of the 64 atoms and the 128 atoms, respectively. The MSD shows a free-particle like behavior until about 0.1 ps and then follows a straight line in a long-time region with excellent statistical accuracy (see figure. 4). The self-diffusion coefficients D's are estimated by the gradient of the MSD for $1 < t < 3$ ps. The results of D are 0.89 $\times 10^{-4}$ and 1.07 $\times 10^{-4}$ cm^{2}s^{-1} for the system 1 and 2, respectively. The VAF's do not take large negative values. This implys that the *cage effect* is small in liquid germanium (see figure 5). The self-diffusion coefficients, D's, estimated from the spectrum of the VAF for the system 1 and 2 are 0.92 $\times 10^{-4}$ and 1.09 $\times 10^{-4}$ cm^{2}s^{-1}, respectively. The self-diffusion coefficient for the system 2 is about 20 % larger than that for the system 1. This means that the periodic boundary condtions may affect the dynamic properties in a small size simulation.

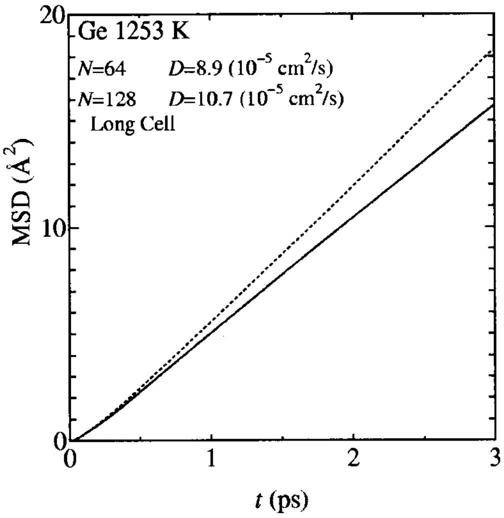

Figure 4. The mean square displacement (MSD) of atoms of liquid germanium at 1253 K. The solid and the dashed lines show the results for the system of 64 atoms and 128 atoms, respectively.

In figures 6 and 7 the dynamic structure factors, $S(Q,\omega)$'s, for $0.2 < Q < 2.8$ Å^{-1} are shown. The solid and the thick dashed lines show the results obtained by the system 1 and 2, respectively. The experimental results [5] are also presented by the open circles (raw data) and the thin dashed lines (fitting curves). The side peak for small Q-region Å^{-1}, which shows a longitudinal propagating mode, is well reproduced by both the systems 1 and 2. With increasing wavenumber Q, the side peak becomes less pronounced. The central peak in $S(Q,\omega)$ becomes sharper and more intense around $Q = 2.5$ Å^{-1}, which is the main peak position of $S(Q)$, that is called de Gennes narrowing. The calculated results are in good agreement with the experimental data for all Q-region.

The dispersion relation was also calculated, which is the relation between Q and the

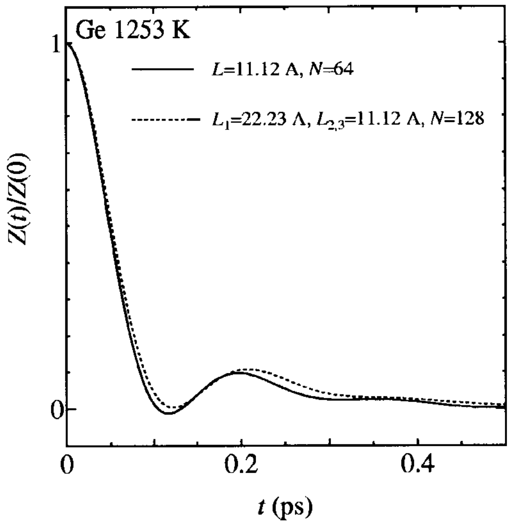

Figure 5. The velocity autocorrelation functions of liquid germanium at 1253 K. The solid and the dashed lines show the results for the system of 64 atoms and 128 atoms, respectively ($Z(t)$: VAF at time t).

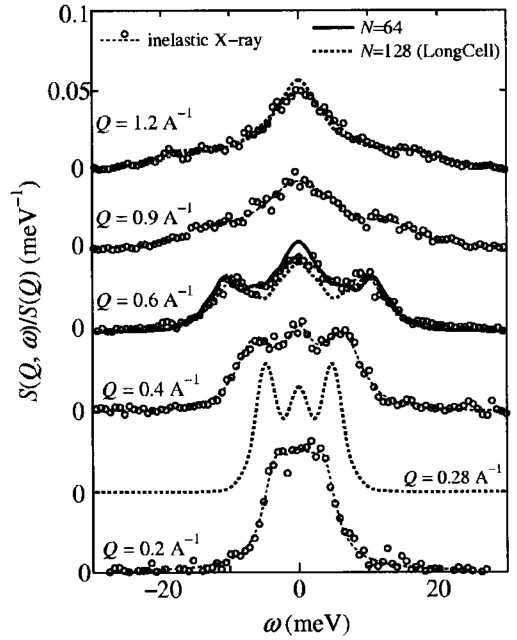

Figure 6. Dynamic structure factor $S(Q,\omega)$, of liquid germanium for $0.2 < Q < 1.2$ Å^{-1} at 1253 K. The solid and the thick dashed lines show the results obtained by the system 1 and 2, respectively. The experimental results [5] are also presented by the open circles (raw data) and the thin dashed lines (fitting curve). $S(Q)$ is the static structure factor.

frequency of the side-peak ω_p. For the system 1 the side peaks are observed only for the two Q values. On the other hand for the system 2 since the five points for $Q = 0.28 \sim 0.84$ Å^{-1} are observed, we can estimate the gradient of the dispersion curves accurately and that agrees reasonably well with the experimental sound velocity 2682 m s^{-1} [13].

4 Summary

The dynamic properties of liquid germanium was investigated by the first-principles molecular-dynamics simulations. It was shown that the long MD cell is effective to investigate long-range correlation function with a small number of atoms. It was also shown that the self-diffusion coefficient for the system of the long MD cell with 128 atoms is about 20 % larger than that for the system of the cubic cell with 64 atoms.

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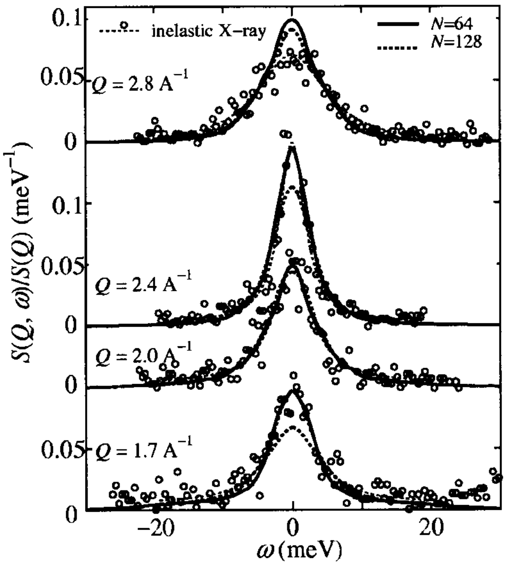

Figure 7. Dynamic structure factor, $S(Q,\omega)$, of liquid germanium for $1.7 < Q < 2.8$ Å^{-1} at 1253 K ($S(Q)$: Static structure factor).

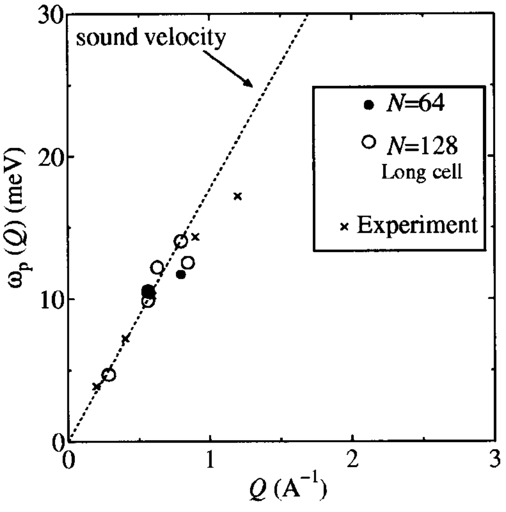

Figure 8. Dispersion relation $\omega_p(Q) - Q$ of liquid germanium. $\omega_p(Q)$: the side peak frequenct of $S(Q,\omega)$ at the wave number, Q. The solid and the open circles show the results for the system of 64 atoms and 128 atoms, respectively. The triangles show the experimental data [5]