

Molecular dynamics simulations of liquid IV-IV alloys

by

Tadahiko Masaki¹ and Toshio Itami¹

Abstract: The partial structure factors of liquid Ge-Sn and Ge-Si are important for the modeling of diffusion phenomena in these liquid alloys. These partial structure factors were calculated by using two kinds of molecular dynamic simulations, *ab initio* molecular dynamics simulation and classical molecular dynamics simulation with the Stelling-Weber interatomic potential. Total structure factors obtained from these molecular dynamics simulations and neutron scattering experiments are in good agreement with each other.

1. Introduction

The atomic configuration of liquid alloys is one of the important subjects for the condensed matter physics. However, three kinds of partial structure factor (PSF) are required for the complete understanding of one alloy. It is almost impossible to obtain these PSF's experimentally. Computer simulation, such as a molecular dynamics simulation, provides us the information of atomic configuration of each atom in liquids and in principle, the PSF's can be obtained from this technique. Nevertheless, the classical molecular dynamics simulations have a problem on the application to liquid alloys because of the ambiguity of interatomic potential.

In the case of liquid IVB metals, Stelling and Weber developed a interatomic potential (SW potential) which includes many body interaction of silicon. This interatomic potential is rather simple but the classical molecular dynamics simulation with this potential well reproduces the structure and properties of liquid silicon and germanium. SW potential has been developed mainly for the simulation of pure liquid Si and Ge. However, it can be applicable for liquid alloys if the interatomic potential between different kind of atoms is assumed in some way.

On the other hand, the *ab initio* molecular dynamics simulation overcomes the problem of classical molecular dynamic simulation, in which the force of atoms can be directly evaluated from the atomic configuration and corresponding electron density in liquid metals without any empirical parameters. In spite of its advantage, however, it is rather not easy to perform this method because of the complexity of program. Therefore, in this research project, we calculate the liquid structures of Ge-Sn and Ge-Si based on *ab initio* molecular dynamic simulations in collaboration with Prof. Hoshino in Hiroshima Univ.

In this year, these two kinds of molecular dynamic simulations were performed for liquid Ge-Si alloys to obtain liquid structures and properties. In this report, the comparison of obtained results between these simulations is introduced briefly together with the results of neutron scattering experiments.

¹Japan Aerospace Exploration Agency, 2-1-1 Sengen, Tsukuba, Ibaraki, 305-8505 Japan

2. Molecular dynamics simulations

2.1 Classical molecular dynamics simulation of liquid Ge-Si alloys

It is well known that the structure of liquid IVB metals shows a characteristic feature, namely the shoulder shape was observed at the high Q side of first peak of S(Q). The origin of this feature has not been clarified. As one of possibilities, the residue of crystal structure, such as a diamond structure, in the liquid is assumed. The interatomic potential which includes the many body interaction must be used for the simulation of such crystalline structure in liquids. The Stellingwerf-Weber interatomic potential is one of the many body interatomic potentials. In this potential the potential energy depending on distances and angles between three atoms are considered, as follows:

$$u(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \sum_{i < j} \phi_2(\mathbf{r}_i, \mathbf{r}_j) + \sum_{i < j < k} \phi_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) + \dots + \phi_N(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$$

$$\phi_2 = \epsilon f_2(r_{ij}/\sigma), \quad \phi_3 = \epsilon f_3(\mathbf{r}_i/\sigma, \mathbf{r}_j/\sigma, \mathbf{r}_k/\sigma)$$

$$f_2(r) = A(Br^{-p} - r^{-q}) \exp[(r-a)^{-1}], \quad r < a$$

$$f_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) = h(r_{ij}, r_{ik}, \theta_{jik}) + h(r_{ji}, r_{jk}, \theta_{ijk}) + h(r_{ki}, r_{kj}, \theta_{ikj})$$

$$h(r_{ij}, r_{ik}, \theta_{jik}) = \lambda \exp[\gamma(r_{ij}-a)^{-1} + \gamma(r_{ik}-a)^{-1}] \left(\cos \theta_{jik} + \frac{1}{3} \right)^2, \quad r_{ij} < a, r_{ik} < a$$

Parameters of this potential are decided based on the properties of crystal at melting point. These parameters for Ge and Si have been presented by several researchers and the molecular dynamics simulations of pure Ge, pure Si and Ge-Si alloys have been studied. In this research, parameters presented by Yu et al.[1] were used for the simulation of partial structures of liquid Ge-50 atomic%Si. In this simulation, the unit cell contained 1728 atoms composed of Ge atoms and Si atoms. The periodic boundary condition was applied. The diamond structure of Ge was constructed as an initial configuration of simulation and a half of atoms are randomly replaced by Si atoms. The time developments of displacement of atoms were calculated due to the Verlet's velocity algorithm. The temperature of simulation was 2000 K. The time step was 0.5 fs and the total time of simulation was 20 ps.

2.2 *Ab initio* molecular dynamics simulation of liquid Ge-Sn and liquid Ge-Si alloys

Ab initio molecular dynamics simulation is one of the most up-to-date methods to obtain the structures and electronic states in liquids theoretically. In the present research, the *ab initio* molecular dynamics simulation is based on the density functional theory in which the generalized gradient approximation is used for the exchange-correlation energy. For the electron-ion interaction, the norm conserving pseudopotentials were used for Ge, Sn and Si. Details of the simulation were described in the previous report of this research project [2].

In this simulation, the super cell contained 64 atoms composed of Ge atoms and Sn or Si atoms, and the periodic boundary was applied for the model of these liquid alloys. The diamond structure of Ge was taken as an initial configuration and some atoms were replaced by Sn or Si atoms whose numbers corresponded to the concentration of alloys. The temperature of simulating system was controlled by the Nose-Hoover method. The initial temperature was kept at higher temperature than the melting temperature for the achievement of liquid state. After that, the temperature was gradually decreased to the target temperature. The simulation was carried out during 9.68 ps with a time step of 0.968 fs for Si-Ge alloys and during 86-102 ps with a time step of 2.7-3.2 fs for Ge-Sn alloys. The temperature of the simulations was 1593K for Si-Ge and 1273K, 1523K and 1773K for Ge-Sn respectively.

3. Results and Discussions

The space and time correlation of atoms in liquids is one of the essential factors to understand the static and dynamic properties of liquid alloys. Especially, correlations between same and different kinds of atoms, such as partial radial distribution function, are important to know the interaction of atoms. A molecular dynamic simulation can be employed as a powerful tool for this subject because these correlation functions are directly calculated from the mean of atomic configuration of each time step.

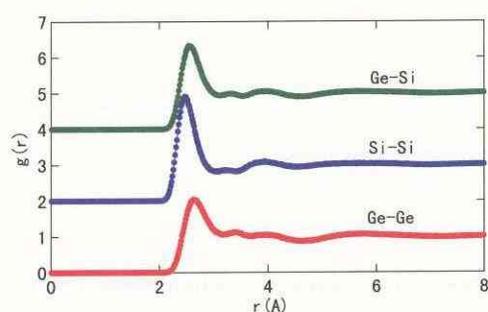


Figure 1 Partial radial distribution function of liquid Ge-50 atomic%Si by classical molecular dynamics simulation with SW potential

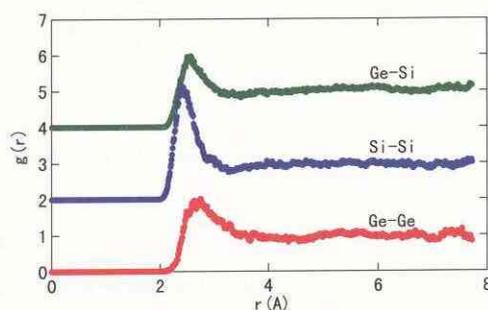


Figure 2 Partial radial distribution function of liquid Ge-50 atomic%Si by *ab initio* molecular dynamics simulation

In the activity of the diffusion project in this year, the static structure of liquid Si-Ge was calculated based on two different kinds of molecular dynamics (MD) simulations, *ab initio* method and the classical method.

The partial radial distribution functions of liquid Ge-Si are shown in figure 1 and figure 2. It can be seen in both cases that the height of the first peak of $g_{\text{Si-Si}}(r)$ was larger than that of $g_{\text{Ge-Ge}}(r)$ and $g_{\text{Ge-Si}}(r)$. Other characteristic features were slightly different. In the results of classical molecular dynamics simulation, the small peaks of $g(r)$ can be seen between the first peak and second one. This additional peak may be derived from the asymmetric term of SW potential. However, in the results of *ab initio* molecular dynamics simulation, such small peaks cannot be observed.

The partial structure factors are obtained from the Fourier transform of these radial distribution functions. The total structure factor is obtained from the sum of these partial structure factors by taking into account both atomic scattering factors and concentration of alloys.

In the case of Ge-50 atomic%Si, the static structure factor was measured by the use of neutron scattering in this project. This was described in our previous report. The static structure factors obtained from the *ab initio* MD and the classical MD can be compared with the experimental result. As shown in figure 3, results of these simulations are in good agreement with that of neutron scattering experiments.

It can be regarded from these results that the classical molecular dynamic simulation with SW potential is one of easily feasible methods to calculate the characteristic feature of total structure factor of liquid Si-Ge alloys. However, it should be carefully applied to the analysis of partial structure factors because details of partial radial distribution functions are different between the classical MD and the *ab initio* MD.

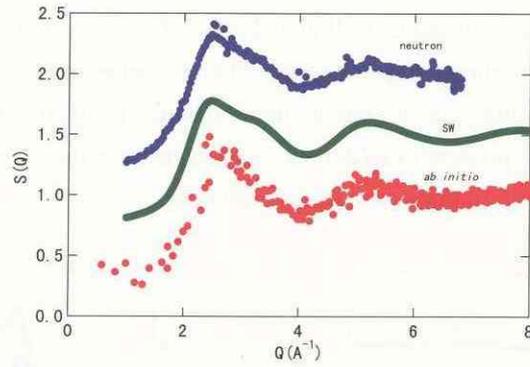


Figure 3 Total scattering factor of liquid Ge-50 atomic%Si

4. Summary

The molecular dynamics simulation is a powerful tool for the analysis structure of liquid metals. The total structure factors of liquid Ge-Si alloy were obtained and those are in good agreement with results of neutron scattering experiments.

Reference

- [1] W. Yu, Z.Q. Wang and D. Stroud, Phys. Rev. B, 54, 13946(1996).
- [2] "Modeling and Precise Experiments of Diffusion Phenomena in Melts under Microgravity" Annual Reports 2002, NASDA-TMR-030005E.