

A many-body force molecular dynamics simulation of liquid Ge

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Abstract

We report the results of molecular dynamics simulations for liquid Ge. The empirical interatomic potential, originally proposed by Stillinger-Weber, which includes two- and three-body interactions, was employed. The diffusion coefficient and the static liquid structure obtained by the simulations were compared with results derived from experiments. The diffusion coefficients estimated by molecular dynamics become smaller than experimental data obtained in microgravity. The radial distribution function resulting from the simulations displays clearly too larger second and third peaks. We tried to adjust the interatomic potential parameter to improve the agreement of liquid structure between simulations and experiments. As a result, the diffusion coefficients became larger and the liquid structure closer to the experimental data.

1. Introduction

Properties in the liquid states of metals and semiconductors are of paramount importance from both scientific and industrial point of view (e.g. metallurgy, crystal growth, etc.). However, there are not enough such data and the liquid is less understood compared with solids and gases. This might be a major reason why no idealized model still exists for liquid. One objective of this work is to establish a diffusion model for liquids across a wide range of complexity.

Since it is necessary to understand the diffusion mechanism or microstructure of the liquid from a scientific point of view, molecular dynamics simulations have been performed to estimate the diffusion coefficient and to study the liquid structure. However molecular dynamics simulations have rarely been compared with experimental values because there are few precise diffusion coefficients. Diffusion coefficients of liquid metals and semiconductors have been measured under both terrestrial and microgravity conditions [1-7]. The order of diffusion coefficient in liquid range from 10^{-9} to 10^{-8} m²/s which is much smaller than the variations observed in viscosity of liquids metal and semiconductors. Therefore, diffusion measurements can be affected even in the presence of a weak convection flow. Froberg *et al.* [2] demonstrated that the diffusion coefficients could be measured in microgravity far more precisely than on the earth. As for liquid Ge, Itami *et al.* with a long capillary method [3] and Yoda *et al.* with a shear cell method [4] have carried out diffusivity measurements of liquid Ge aboard a TR-IA Japanese sounding rocket. These experiments were the first attempt to measure the diffusion coefficients of liquid Ge in microgravity.

The diffusion coefficient is a macroscopic property and cannot provide us the microscopic information. We need to know microscopic information such as the dynamic motion of atoms or the liquid structure in order that we may clarify the diffusion mechanisms and establish a diffusion model. Therefore, we carried out molecular dynamics simulations and compared the result of the diffusion coefficient and liquid structures with experimental data. In this paper, the results of molecular dynamics simulations for liquid Ge are reported. The diffusion coefficients and the static structure are discussed.

Table 1 Values of modified SW potential parameters for Ge [8]

A	6.768571075	σ (Å)	2.181	p	1
B	0.616574299	λ	8.37	γ	1.2
ϵ (eV)	1.93	δ	0.9625	b	1.8

2. Molecular dynamics simulations

2.1 Interatomic potential

The structure of the crystalline state of Ge is a four-coordinated diamond lattice. A lot of empirical potentials of Si and Ge have been proposed for various phases. The empirical interatomic potentials are taken to be sums of two- and three-body potentials originally proposed by Stillinger and Weber. Modified Stillinger and Weber (SW) potential has reproduced many properties of both crystalline and liquid phases. Jian *et al.* [8] noticed that the SW potential does not satisfy the phonon-dispersion relations. Therefore, the modified SW potential is adopted. The explicit form is as follows;

$$\phi = \phi_2 + \phi_3 \quad (1)$$

$$\phi_2(r_{ij}) = \epsilon f_2(r_{ij}/\sigma) \quad (2)$$

$$f_2(r) = \begin{cases} A(Br^{-p} - 1) \exp[\delta / (r - b)] & r < b \\ 0 & r \geq b \end{cases} \quad (3)$$

$$\phi_3(r_i, r_j, r_k) = \sum f_3(r_i/\sigma, r_j/\sigma, r_k/\sigma) \quad (4)$$

$$f_3(r_i, r_j, r_k) = h(r_{ij}, r_{ik}, \theta_{jik}) + h(r_{ji}, r_{jk}, \theta_{ijk}) + h(r_{ki}, r_{kj}, \theta_{ikj})$$

$$h(r_{ij}, r_{ik}, \theta_{jik}) = \lambda \exp\left[\gamma(r_{ij} - b)^{-1} + \gamma(r_{ik} - b)^{-1}\right] \left[\cos \theta_{jik} + \frac{1}{3}\right]^2, \quad \lambda > 0 \quad (5)$$

where ϕ_2 and ϕ_3 represent the two- and three-body interactions, respectively. A , B , ϵ , p , q , λ , and γ are adjustable parameters listed in Table 1. The distance r_{ij} is defined as $|r_i - r_j|$. σ is chosen to make f_2 a minimum at $r = 2^{1/6}$. θ_{jik} is the angle subtended by r_{ij} and r_{ik} with the vertex at i . The three-body interaction becomes zero at $\theta_{jik} = 109.5^\circ$ which is the angle of a perfect tetrahedron.

2.2 Simulation procedure

We employed a canonical (N , V , T) ensemble in which the total number of atoms N , volume V , and temperature T are held constant. A periodic boundary condition on a simple cubic cell is put on the three-direction boundary. We use the 5th order predictor-collector (Gear) algorithm to integrate the Newtonians equation of motion. The time step is 0.5 fs and the number of iteration is 10^5 except at the initial relaxation time. We carried out simulations changing the number of atoms in the calculation cell. The estimated diffusion coefficients showed the dependence on the number of atoms and when more than 2744 atoms are contained, it is almost constant within 1.8%. To reduce the calculation time, we employed 2744 atoms. The temperature is changed from 1250 to 1800 K and the density is reduced with increasing temperature. We reviewed the previous density measurements of liquid Ge. The temperature dependence of density is shown in Fig. 1 [9-14]. The later measurements tend to have larger density. We used the temperature dependence of the density measured by Nakanishi *et al.* [10] with dependency on temperature, which is represented as follow;

$$\rho(T) = -0.442T + 6.17 \times 10^3 \quad \text{kg/m}^3 \quad (6)$$

where ρ is density and T temperature.

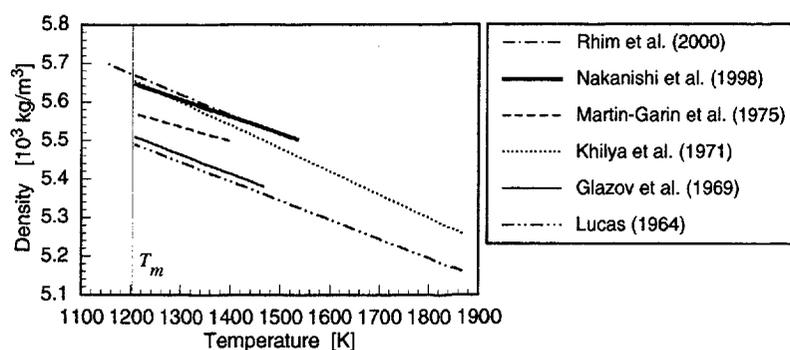


Fig. 1 Temperature dependence of density of liquid Ge [9-14]. The density measured by Nakanishi *et al.* [10], represented by the bold line, is used in the simulations.

3. Results and discussions

We estimated the diffusion coefficient from the mean square displacement. The diffusion coefficient is represented in Fig. 2 as a function of temperature. Experimental results which were performed both on the ground (1G) [1] and in microgravity (μ G) [3, 4] are also plotted in Fig. 2. Diffusion coefficients from molecular dynamics simulations are smaller than experimental results that have a slightly steep slope of temperature dependence. Figure 3 shows the radial distribution function. The second and third peaks appear too large although the experiment [15] revealed broad and low intensity peaks. It seems that a four-coordinated lattice structure in the solid still remains important since the three-body interaction may be too strong.

Since the parameters of the Stillinger-Weber potential was empirically adjusted to reproduce the bonding energy at the melting point, T_m , we think that a three-body potential acts too strong in liquid states. Hence, we tried to decrease the value of the parameter λ appearing in the three-body term. The effect of parameter λ on diffusion coefficient is illustrated in Fig. 4. The diffusion coefficients become larger when decreasing the there-body potential parameter and the second and third peaks in the radial distribution function become smaller and broader (Fig. 5). In the case of a temperature just above the melting point, 1253 K, it seems suitable to set the parameter λ to be 0.8. But now, we cannot express the experimental temperature dependence of diffusion coefficient with any reduced parameter λ . The potential modification should be done by comparing the liquid structure obtained from simulations and that from experiments. There are few structure data for liquid Ge at high temperature. X-ray and/or neutron scattering characterization of the liquid structure is warranted in a near future.

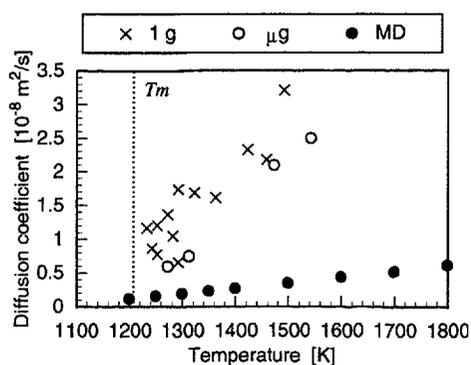


Fig. 2 Temperature dependence of diffusion coefficient

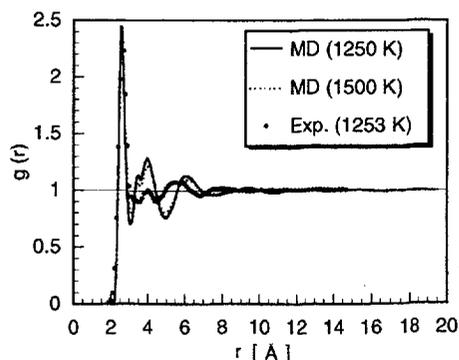


Fig. 3 Radial distribution function. Experimental data are from Ref. 15.

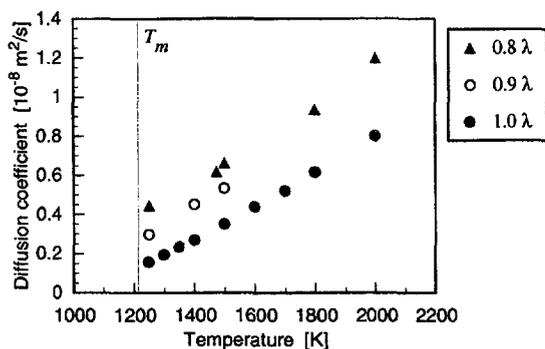


Fig. 4 Effect of three-body potential parameter, λ

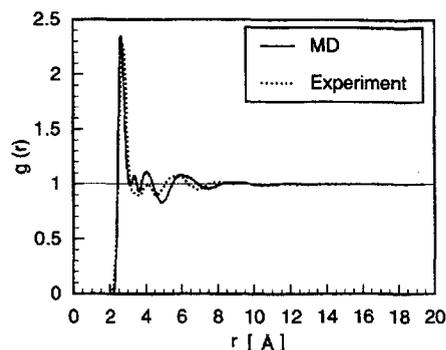


Fig. 5 Radial distribution function with modified potential parameter, $\lambda = 0.8$

4. Summary

We carried out molecular dynamics simulation for liquid Ge based on the many-body potentials. The modified Stillinger-Weber potential is employed as the empirical interatomic potential. The diffusion coefficients and the liquid structure were compared with experimental data. It was found that the diffusion coefficients obtained by the simulations were smaller and had gentler slope of temperature dependence than obtained from experiments. The three-body potential parameter was changed to weaken the three-body forces. As a result, the diffusion coefficient was close to experimental data and the structure was consistent with X-ray scattering data taken at 1253 K. More simulation work is needed to reveal why the diffusion coefficients exhibit a strong temperature dependence and to understand the diffusion mechanisms.

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