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分子動力学法を用いた液体金属における原子の自己拡散挙動評価

Self-diffusion Behavior of Atoms in Liquid Metals Using Molecular Dynamics Simulation

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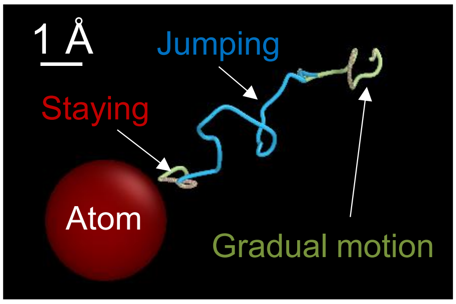
Abstract: The objective of this study is to clarify each contribution of atomic microscopic motion to self-diffusion coefficients in liquid metals. Molecular dynamics simulations of liquid Al, Sn and Pb were performed using polynomial machine learning potential. The simulation reproduced experimental results under microgravity conditon sufficiently. Atomic motion was classified into juming motion, gradual motion and staying state from the time evolution of speed of each atom using the first peak position of the pair distribution funciton in each element. The self-diffusion coefficients were formulated using squared displacement and frequency of each motion with the correction of oscillation around the same place. The relative errors of the calculated self-diffusion coefficients were 25-40 % without the correction and were minimized to 3-7 % with the correction. The contribution of gradual motion to the self-diffusion coefficient was the largest among the three classifications.



Keywords: Liquid metals, Diffusion coefficient, Molecular dynamics simulation, Jump diffusion

1. Introduction

Diffusion coefficients in liquid metal is an important physical property for solidification simulation. In the previous studies, jumping motion, which means an atom moves significantly in almost the same direction, is suggested in liquid metals[1-3)] using Molecular Dynamics (MD) simulation. Our research group has established a method to classify atomic motion into jumping, gradual motion and staying[4)]. However, it has not been clear how such motions affect self-diffusion coefficient quantitatively. This study aims to clarify contribution of each atomic motion to a self-diffusion coefficient.

2. Computational procedures

The MD simulations of liquid Al, Sn and Pb were performed. The calculations were carried out with polynomial machine learning potential[5)]. In each element, 4000 atoms were initially arranged in a cubic simulation box which had an fcc structure under periodic boundary conditions. Each atom was given a serial number (ID). After the equilibration process, the simulations for self-diffusion calculation were performed for 1 fs×100000 steps for Al, and for 2 fs×100000 steps for Sn and Pb under NVT (constants of the number of atoms, volume, and temperature) ensemble. The temperature was set as 973 K for Al and 773 K for Sn and Pb corresponding to the reference self-diffusion measurements.

After the simulation, the pair-distribution function and the position of the first-peak l_0 was calculated. The time evolution of speed was also calculated in each atom and its time range was divided into several sections, as following the suggested method[4]. If the length of the straight line from start to end of a section was longer than l_0, the section was judged as jumping section. If there is no local minimum value of speed in the section, the section was judged as staying section. The other sections were judged as gradual motion sections.

3. Results

The self-diffusion coefficients D_{MSD} were calculated from mean square displacement (MSD) as 6.7×10^{-9} m^2s^{-1}, 6.6×10^{-9} m^2s^{-1} and 3.0×10^{-9} m^2s^{-1} for Al, Sn and Pb, respectively. The relative errors of the calculated self-diffusion coefficients from the reliable experimental results from the conditions on the ground[6-8] and under the microgravity[9-11] were within 30 %. Because the calculated and experimental results are of the same order, these calculations are considered to have reproduced the experimental results sufficiently.

The first-peak position of pair distribution function was calculated as 2.77 Å, 3.15 Å and 3.37 Å for Al, Sn and Pb, respectively. **Figure 1** shows the divided period and atomic trajectory during the time range from 2000 fs to 4000 fs of ID 1 in Al.

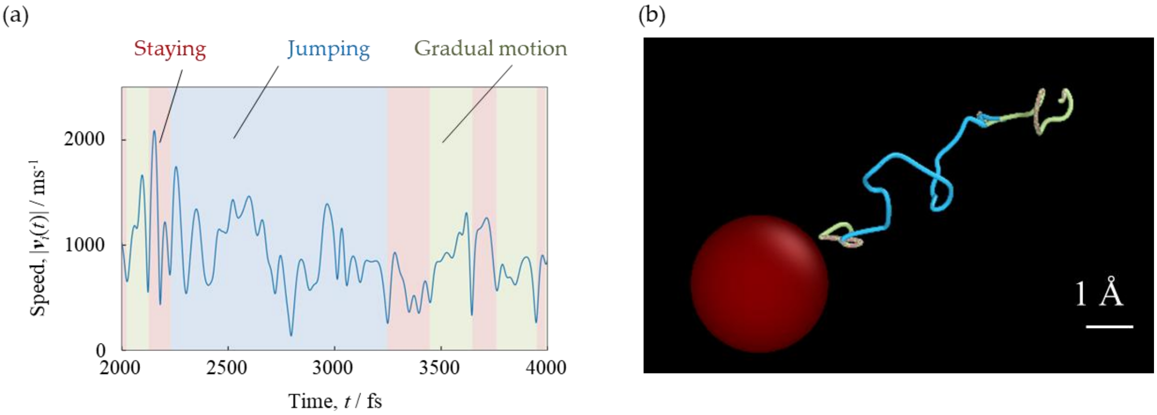


Figure 1. Time evolution of speed and atomic trajectory from 2000 fs to 4000 fs. (a) Time evolution of speed and divided time of ID 1. (b) An atom (red sphere) and atomic trajectory during the time range. Each color corresponds to the time range in (a). Visualized by OVITO[12].

4. Discussion

In solid state, diffusion coefficients are calculated using **Eq. (1)**, because the atomic motion other than jumping does not contribute to diffusion. In liquid state, considering the additivity of MSD, if all atomic motions contribute to the diffusion coefficient, it can be expressed as in **Eq. (2)**. However, the distance between start and end of the position of each section includes the effect of oscillations around the same place. The diffusion coefficient where the effect of the oscillation around the same place was subtracted was calculated using **Eq. (3)**.

$$D = \frac{\langle L_{jump}^2 \rangle}{6} \Gamma_{jump} \tag{1}$$

$$D_{calc} = \frac{\langle L_{jump}^2 \rangle}{6} \Gamma_{jump} + \frac{\langle L_{gradual}^2 \rangle}{6} \Gamma_{gradual} + \frac{\langle L_{stay}^2 \rangle}{6} \Gamma_{stay} \tag{2}$$

$$D_{calc} = \frac{\langle L_{jump}^2 \rangle - \langle L_{oscillate}^2 \rangle}{6} \Gamma_{jump} + \frac{\langle L_{gradual}^2 \rangle - \langle L_{oscillate}^2 \rangle}{6} \Gamma_{gradual} + \frac{\langle L_{stay}^2 \rangle - \langle L_{oscillate}^2 \rangle}{6} \Gamma_{stay} \tag{3}$$

L_{jump} : Distance from start to end of the positions of a jumping motion (m)
$L_{gradual}$: Distance from start to end of the positions of a gradual motion (m)
L_{stay} : Distance from start to end of the positions of a staying state (m)
$L_{oscillate}$: Distance from the position an atom receives a repulsive force to that the atom receives a repulsive force again (m)
Γ_{jump} : Frequency of jumping motion (s^{-1})
$\Gamma_{gradual}$: Frequency of gradual motion (s^{-1})
Γ_{stay} : Frequency of gradual staying state (s^{-1})

The relative error of the self-diffusion coefficient was calculated using **Eq. (4)**.

$$\Delta D_{calc} = \frac{D_{calc} - D_{MSD}}{D_{MSD}} \tag{4}$$

Here, ΔD_{calc} denotes relative error. The relative errors of the self-diffusion coefficients calculated using **Eq. (2)** were 40 %, 25 % and 33 %, and that calculated using **Eq. (3)** were 3.5 %, 6.7 % and 6.4 % for Al, Sn, and Pb, respectively. Therefore, the effect of oscillation should be corrected. Defining each term in **Eq. (3)** as D_{jump}, $D_{gradual}$ and D_{stay} from start respectively, the ratio of $D_{gradual}$ to D was the largest in all elements. Thus, the gradual motion is considered to have been largest contribution to self-diffusion coefficients.

5. Conclusions

The self-diffusion coefficient was formulated using three terms, which mean diffusion coefficients of staying state, gradual motion and jumping motion with the correction of oscillation around the same place for each term. The relative errors of the calculated diffusion coefficients were 25-40 % without the correction and were minimized to 3-7 % with the correction. The contribution of gradual motion to a self-diffusion coefficient was the largest.

Acknowledgments

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Conflict of Interest

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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