Molecular dynamics simulations for liquid lithium

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Abstract

The molecular dynamics simulation was performed for liquid Li with realistic interionic potentials, which were derived from the pseudopotential theory. The obtained self-diffusion coefficients were in good agreement with those obtained by the microgravity rocket experiment. The refined hard sphere theory was also applied for the theoretical calculation of self-diffusion coefficient. Obtained results were in good agreement with microgravity experiment in the low temperature range though some difference was observed in higher temperature range. From the velocity auto-correlation function the mechanism of the diffusion was discussed.

1. Introduction

The precise measurement of the diffusion coefficient in melts is one of the most important themes in the field of microgravity utilization. In molten materials, the existence is presumed for the particular short range order or chemical short range order. The diffusion behavior in melts seems to be influenced deeply by this kind of particular short range order. Recently, much attentions have been focused on the melts of metals, alloys and semiconductors because these melts are regarded as complex liquids with particular short range order or chemical short range order rather than simple liquids with a random assembly of atoms. We performed the molecular dynamics simulation for liquid Li to analyze the experimental results of TR-1A sounding rocket.

2. Numerical modeling and calculation method

We performed the classical molecular dynamics simulations(MD) for liquid Li. Employed interionic potential was derived from the pseudo potential theory with the Ashcrott empty core model potential and the Vashsta-Singwi or Ichimaru-Utsumi dielectric screening function. The same potential was used in the calculation of the refined hard sphere model based on the Weeks-Chandler-Andersen(WCA) perturbation theory of liquids.. The explicit form is shown in Fig.1. The classical MD simulations with 1458 particles were performed for liquid Li under the condition of canonical ensemble. The density at each temperature was determined by the experimental data, shown in Fig.2.

3. Results and discussions

3.1 Structure of liquids

The structure of liquid Li was analyzed in the forms of both the radial distribution function and the structure factor; the latter is the Fourier transform of the former. They are shown in Figs.3 and 4, respectively.

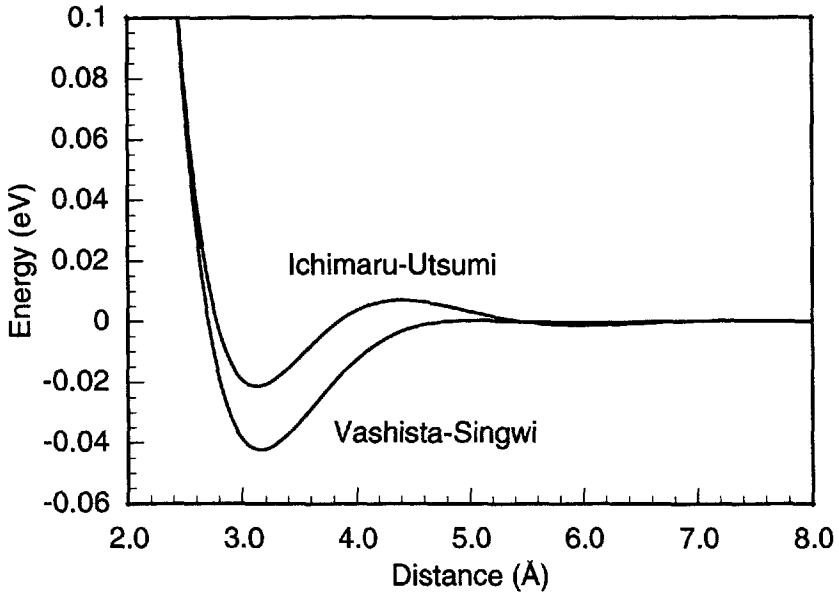

Fig.1 Interionic potential of liquid Li at the melting point

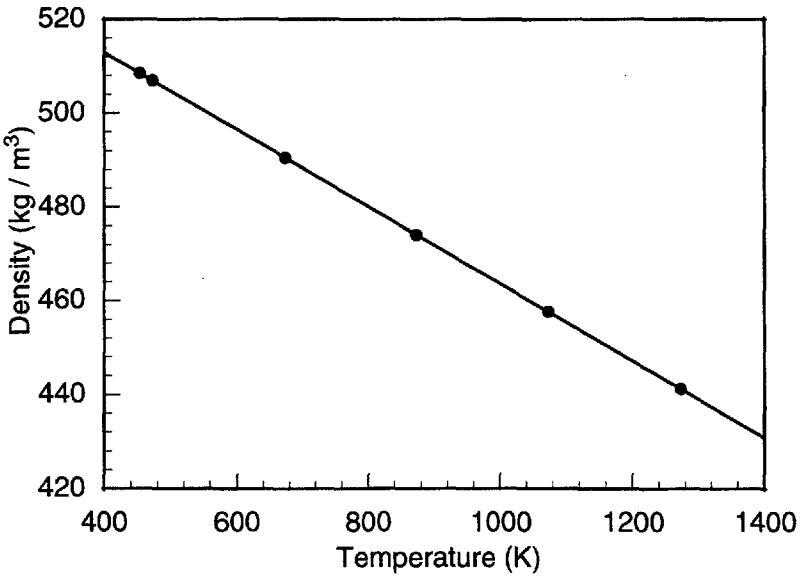

Fig.2 Dependence of density of liquid Li on the temperature

The structure factor at the melting point agrees closely with the result of neutron scattering by N. S. Gingrich.[1] Therefore, there is a considerable reliability in the present simulation and the interionic potential employed.

3.2 Analysis of diffusion process in liquid Li and comparison among the microgravity experiment, MD simulations and the refined hard sphere theory

At first, we evaluated the diffusion coefficient from the time development of the mean square displacement of atoms.

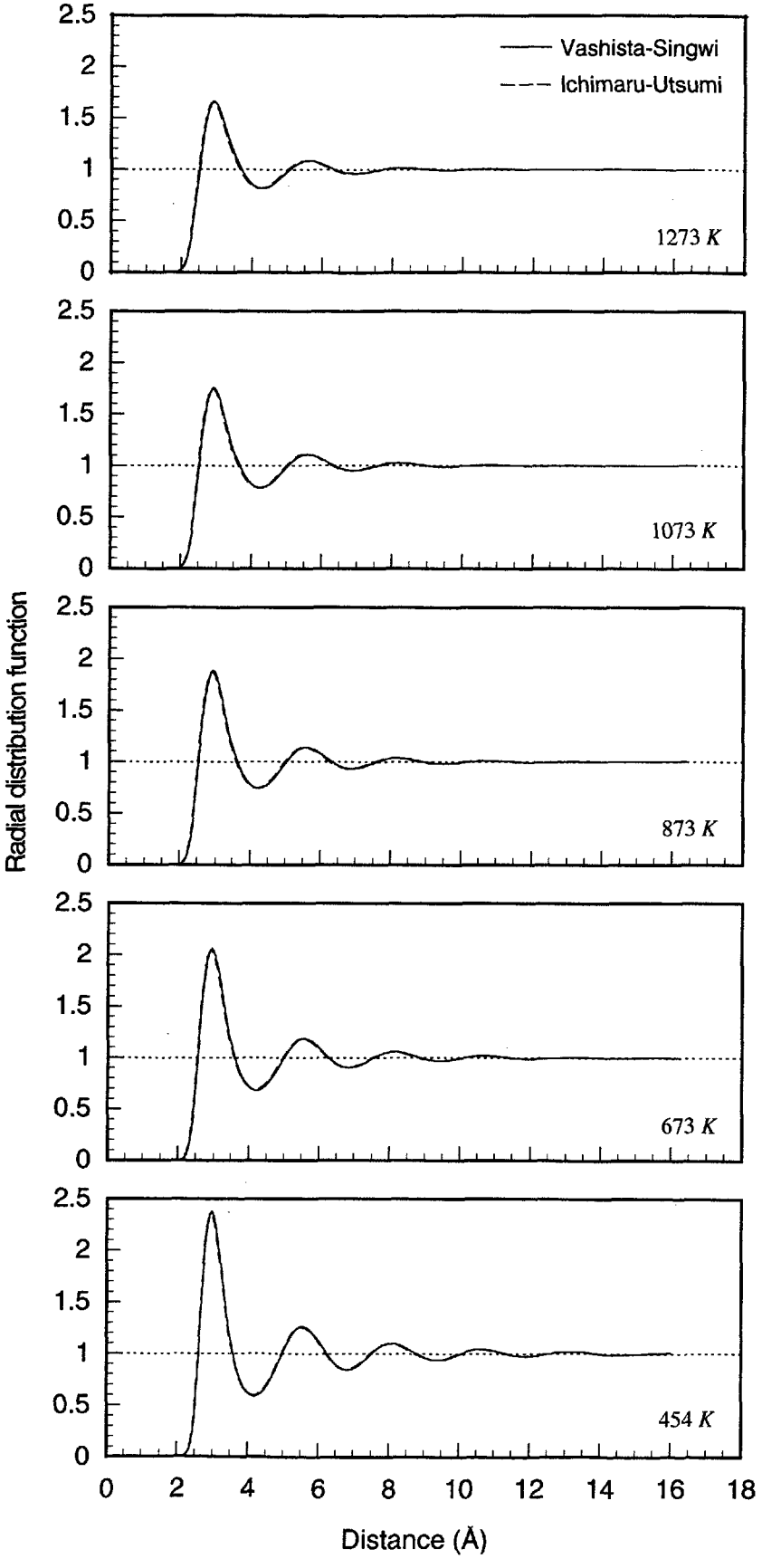

Fig.3 Radial distribution function of liquid Li

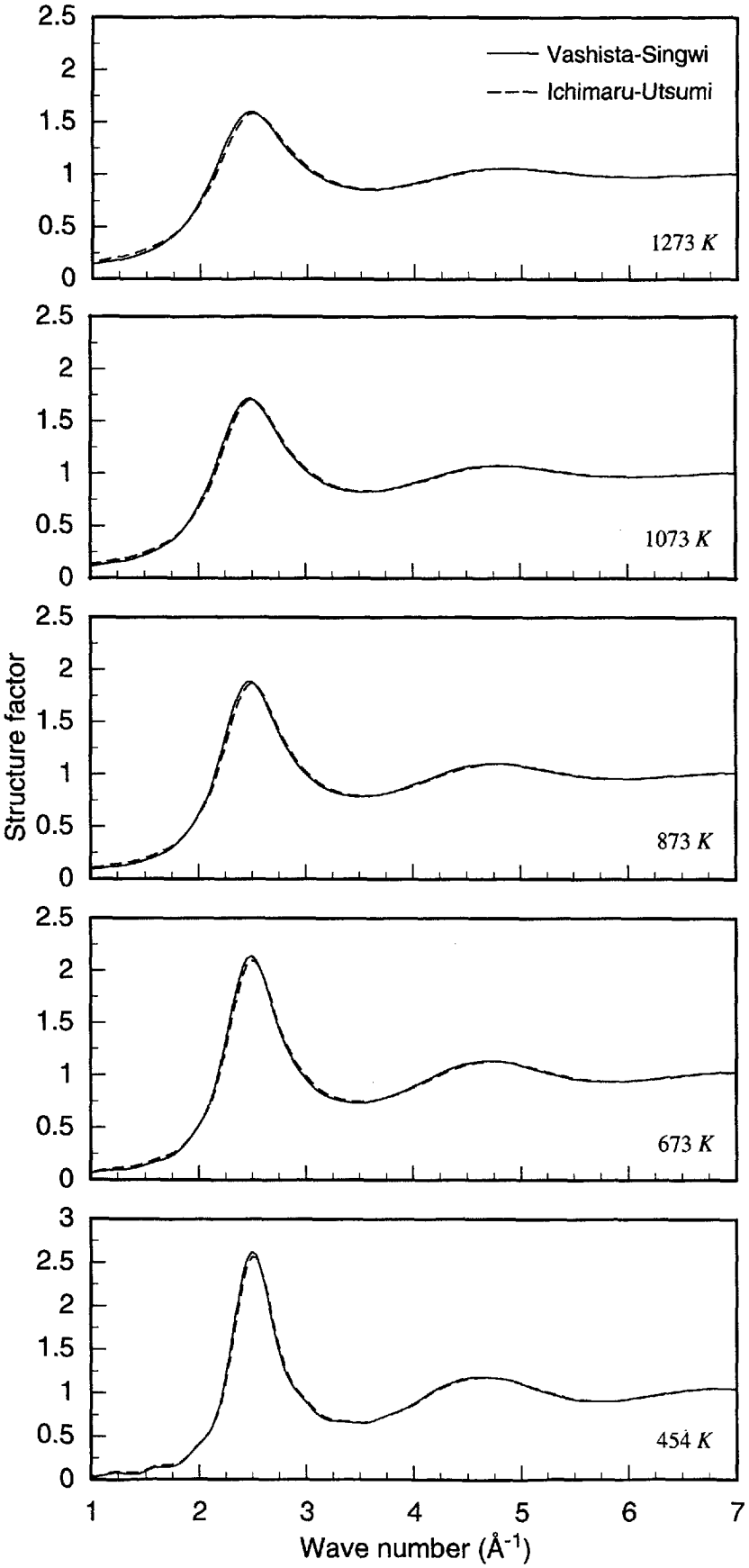

Fig.4 Structure factor of liquid Li

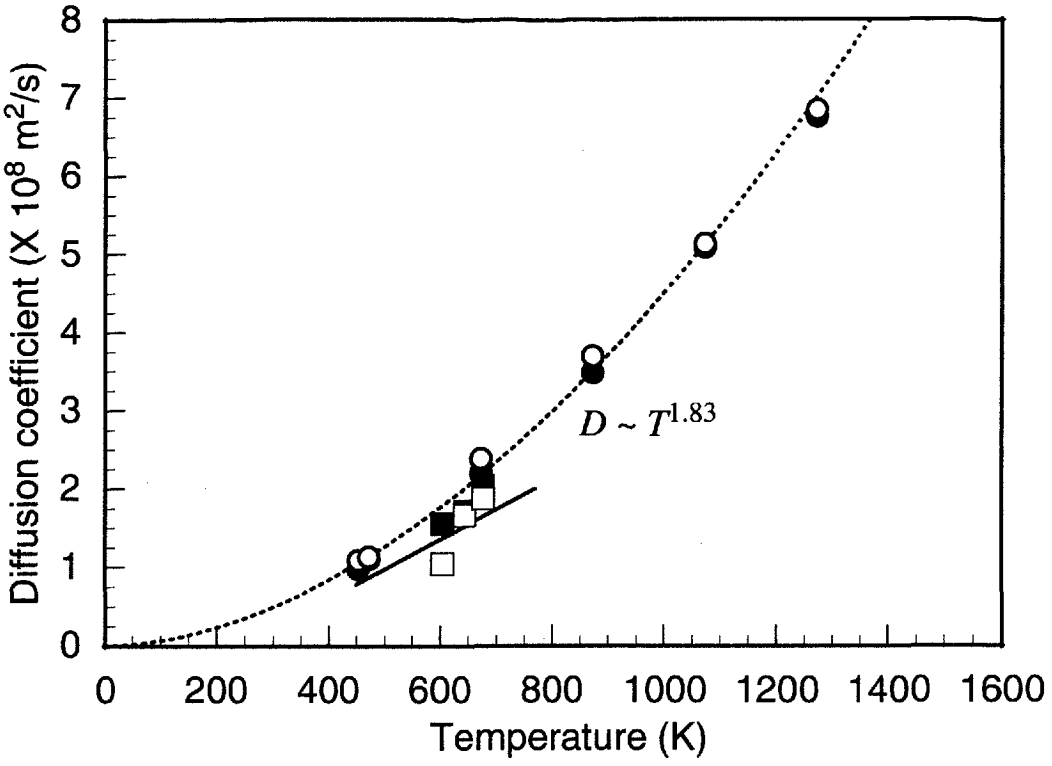

Fig.5 Dependence of the self-diffusion coefficient in liquid Li on the temperature
● : MD (Vashista-Singwi) , ○ : MD(Ichimura-Utsumi), ■ : TR-IA No.6(^{6}Li),
□ : TR-IA No.6(^{7}Li), : WCA method (Vashista-Singwi).

The dependence of the self-diffusion coefficient on temperature was shown in Fig.5. The experimental data obtained under microgravity (TR-IA No.6) and results of refined hard sphere theory (WCA) are also plotted in Fig.5.

The self-diffusion coefficients from MD simulations well agree with the experimental results obtained by microgravity diffusion experiments. The refined hard sphere theory(WCA) well explains the self-diffusion obtained by this MD simulation and μg experiment in the temperature region of 450~750K, but the discrepancy between the theory and experimental results became larger at high temperature. The difference was discussed from the behavior of the velocity auto-correlation function(VAF). Fig.6 shows the time dependence of the VAF of liquid Li obtained by the present MD simulations. There were characteristic oscillations around zero in the behavior of VAF as a function of time. In the hard sphere system, such long time oscillations in the VAF can not be observed though the negative region in the VAF can be observed surely for the high packing density. In the low packing density range of the hard sphere assembly a rather simple exponential decay behavior can be observed in the VAF. Therefore, the obvious difference of the kinetics of microscopic atomic motion is present between the MD simulations with realistic interionic potentials(or real system) and the hard sphere system. However, there is still some similarity among them; at least the negative range of VAF appears for both approaches. This negative value and the long time tail of

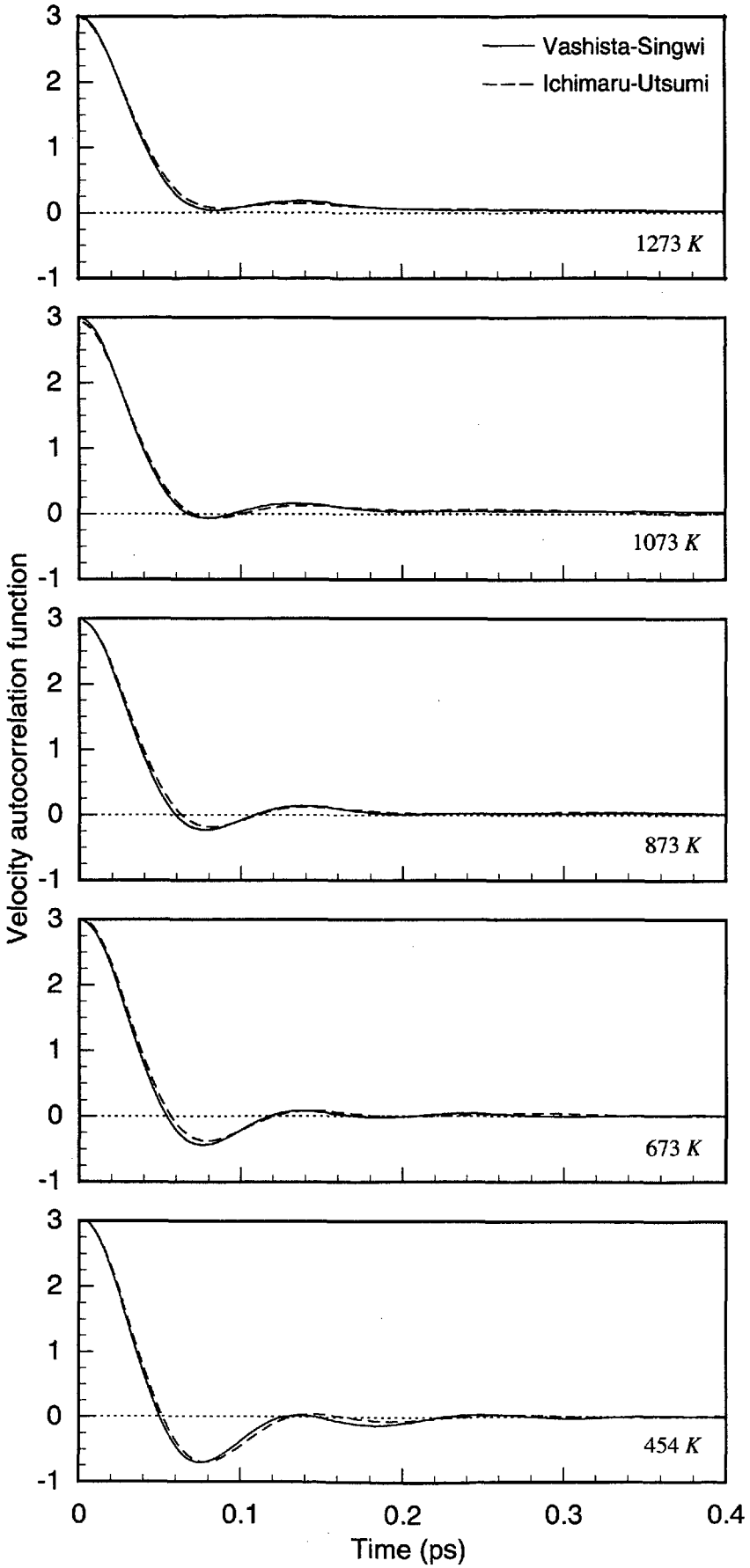

Fig.6 Velocity autocorrelation functions of liquid Li

VAF are considered to be the backward motion of diffusing atoms under the influence of interionic potentials of surrounding atoms. Recently this long time tail behavior has been rigorously analyzed by the mode coupling theory, in which the memory function for the VAF in the generalized Langevin equation is considered to be the superposition of the short time term of hard sphere collisions and long time viscous term. However, its realistic application has been rather limited to the simple liquid metals with well defined interionic potentials. For complex liquids, it is not always easy to define the interionic potential rigorously though the application of mode coupling theory is a challenging future problem.

In the hard sphere model, the similar effect to the long time viscous term in the mode coupling theory is taken into account simply by means of the back scattering factor. The merit of the hard sphere model is its simplicity with only one characteristic parameter, hard sphere diameter or packing fraction. In addition, to this simplicity, many analytical solutions are available for many physical quantities. Therefore, the hard sphere model is a good tool for grasping the gross feature of liquids even in the case of complex liquids, which is essentially extremely complicated many-body problems. It is important to develop the model of diffusion in complex liquids from both the global approach and the detailed approach in order to clarify the essential features in the mechanism of diffusion.

4.Conclusions

In this study, we performed the MD simulations of liquid Li and the results were compared with both the refined hard sphere theory(WCA) and microgravity experiments. The results of self-diffusion coefficient well agreed with the microgravity experiments. The diffusion coefficient obtained by the refined hard sphere model was close to the MD simulation results in the temperature range of 450~750K. There were, however, some differences between them at high temperatures. The limitation and the validity of the hard sphere model were discussed for the application to complex liquids.

[References]

1) N. S. Gingrich et al., J. Chem. Phys., 48, 4838 (1968)