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TRANSPORT PROPERTIES OF SILICATE MELTS ESTIMATED BY MOLECULAR DYNAMICS SIMULATION

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Synopsis

The applicability of molecular dynamics simulation to the transport properties of molten Na_2O-SiO_2 system was investigated. The calculated values of self-diffusivity of each element were in fairly good agreement with the experimental data, but the agreement is relatively poor in the case of shear viscosity. These results are considered to be caused by the limitation in both length and time scales concerning to the dynamics reproduced by the MD simulation.

Key words: molecular dynamics; transport property; self-diffusion; viscosity; thermal conductivity; sodium silicate.

1. Introduction

Transport phenomena in slag play important roles in the field of pyro-metallurgy as the rate determining factors in various processes. There have been carried out many measurements on the shear viscosity, thermal conductivity, and self-diffusivities of ions for many slag compositions including alkali-silicates and alkali-alminosilicates. At the present time, unfortunately, theoretical approaches for the transport properties in such compositions were not so successful in explaining the complicated temperature and compositional dependencies. Hence purely empirical formulations have been used for the evaluation of the transport properties of desired composition and temperatures.

After the study of Woodcock *et al.* [1] on silica glass in 1976, molecular dynamics (MD) simulation has been expected as an useful tool for predicting the properties of slags. It has has been applied to several composition related to slags in both glassy and molten states, and succeeded to reproduce the experimental structures obtained by X-ray diffraction, neutron diffraction, and Raman Scattering. In the case of the transport properties, the self-diffusivity of ion is most frequently investigated. For example, Soules [2] calculated the temperature dependence of the self-diffusivity of oxygen in SiO_2, B_2O_3, and $Na_2O \cdot 3SiO_2$ melts. Angell *et al.* [3] estimated the pressure dependence of self-diffusivity of each constitutional element in SiO_2, $Na_2O \cdot 3SiO_2$, and $Na_2O \cdot SiO_2$ melts. However, there are very

Table 1. Interatomic potential parameters used in this study.

i	a_i /nm	b_i /nm	Z_i
O	0.1629	0.0085	–2.0
Si	0.1012	0.0080	4.0
Na	0.1260	0.0080	1.0

few reports on the compositional dependence and on other transport properties of the melts related to slags. In our previous study [4], we calculated the shear viscosity of $Na_2O \cdot 2SiO_2$ melt at 1000-4000K and showed that the MD simulation has a potential to evaluate the temperature dependence of shear viscosity semi-quantitatively.

The main purpose of this paper is to show the results of MD simulation [5] on the compositional dependencies of transport properties of Na_2O-SiO_2. We deal with three transport properties; self-diffusivity, shear viscosity and thermal conductivity, which play important roles in the metallurgical and other engineering processes at high temperatures.

2. Molecular dynamics simulation

In the MD simulation, transport properties in a liquid can be calculated from autocorrelation of related properties; for example the velocity of atom for self-diffusivity. The formulae used for the evaluation of self-diffusivity D, shear viscosity η, and thermal conductivity λ are given by [6],

$$D = \frac{1}{3N}\int_0^\infty \sum_i^N <\dot{\boldsymbol{r}}(t)\cdot\dot{\boldsymbol{r}}(0)>\mathrm{d}t\ , \tag{1}$$

$$\eta = \frac{1}{3Vk_\mathrm{B}T}\int_0^\infty \sum_{\alpha\beta} <\sigma^{\alpha\beta}(t)\cdot\sigma^{\alpha\beta}(0)>\mathrm{d}t\ , \tag{2}$$

$$\lambda = \frac{1}{3Vk_\mathrm{B}T^2}\int_0^\infty <\boldsymbol{J}(t)\cdot\boldsymbol{J}(0)>\mathrm{d}t\ , \tag{3}$$

where $\boldsymbol{r}_{i}$· is the position of atom i, V the volume of the basic cell, k_B the Boltzmann constant, T the temperature, and $\alpha\beta$ takes the permutation of xy, yz, and zx. The properties $\sigma^{\alpha\beta}$ and $\boldsymbol{J}$ are the microscopic stress and the energy current defined by,

$$\sigma^{\alpha\beta}(t) = \sum_{i=1}^N \left\{ m\dot{r}_i^\alpha(t) r_i^\beta(t) + \frac{1}{2}\sum_{j\neq i}^N F_{ij}^\alpha(t) r_{ij}^\beta(t) \right\}, \tag{4}$$

$$\boldsymbol{J}(t) = \sum_{i=1}^N \dot{\boldsymbol{r}}_i(t) \left\{ \frac{1}{2} m_i \left(\dot{\boldsymbol{r}}_i(t)\right)^2 + \frac{1}{2}\sum_{j\neq i}^N \phi\left(r_{ij}(t)\right) \right\} + \frac{1}{2}\sum_{i=1}^N\sum_{j=1}^N \dot{\boldsymbol{r}}_i(t)\cdot\boldsymbol{r}_{ij}(t)\boldsymbol{F}_{ij}(t), \tag{5}$$

where m_i is the weight of atom i, and F_{ij} the force acting on atom i from atom j.

The interatomic potential used in this study is the Born-Mayer-Huggins form:

$$\phi_{ij}(r) = f_0 (b_i + b_j) \exp\left(\frac{a_i + a_j - r}{b_i + b_j}\right) + \frac{Z_i Z_j e^2}{4\pi\varepsilon_0 r}, \tag{6}$$

where r is the separation between i and j species, ε_0 the dielectric constant, e the electron charge, Z_i the valence of ion i, and $f_0 = 6.9472\times10^{-11}$N. We adopt the values of parameters, a_i, b_i and Z_i, originally determined by Kawamura [7] as listed in Table 1. The validity of these values on the liquid structures were already discussed elsewhere [4,7].

The simulated compositions were selected in the acid range of xNa$_2$O-(1–x)SiO$_2$ system as x = .18, .24, .30, .36, .42 and .50. The MD simulation was carried out by using the Verlet algorithm [6] with the time step of 2fs and 1200 atoms at random initial positions. The periodic boundary conditions were applied to the basic cell, and the long range forces, energy, and the microscopic pressure tensor were calculated by means of the Ewald summations [6]. Simulation was started from 6000K followed by the cooling with the rate of 2K/step to 2000K. Transport properties were estimated by the sampling data in the the constant NVT simulation [9] at 2000K for 20ps. The dimensions of the basic cell for each sample were adjusted so as to attain the experimental density values [8], and the resultant size of the cell is about 2.6nm.

3. Results

In fig. 1 we show the simulated autocorrelation functions of $<v_i(t)\cdot v_i(0)>$ for each elements in .36Na$_2$O–.64SiO$_2$ melt as examples. The network forming ions (Si and O) and network modifying ion (Na) show completely different characteristics to each other. The velocity autocorrelation function of sodium atom shows a monotonous decrease from 0 to 0.1ps followed by one or two weak oscillation and the correlation almost disappears at t > 0.4ps. In the cases of oxygen and silicon atoms, on the other hand, more than ten oscillations were observed up to about 0.4ps which is considered to be caused by the thermal vibration of Si-O bonding. These result suggest that a sodium atom moves in a wider area compared with those for oxygen and silicon atoms.

In fig. 2 are shown the simulated values of $<\sigma^{\alpha\beta}(t)\cdot\sigma^{\alpha\beta}(0)>$ and $<J(t)\cdot J(0)>$

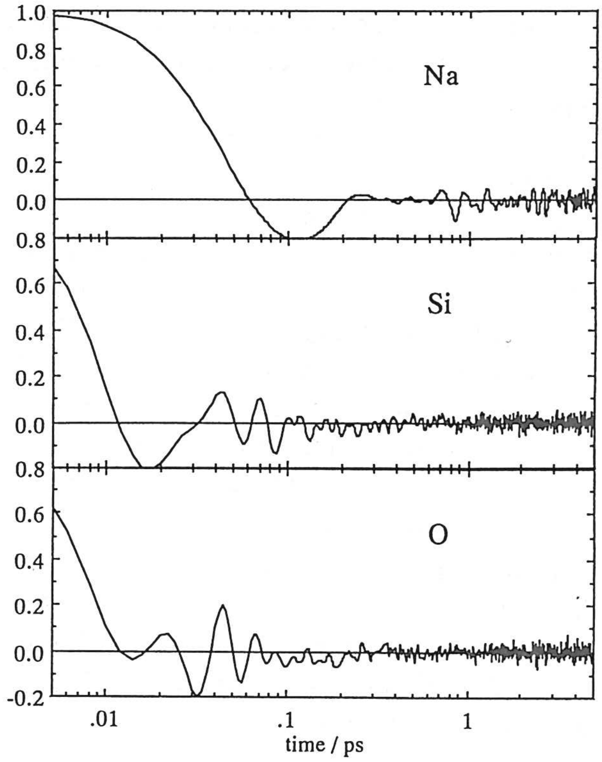

Fig. 1 Normalized velocity autocorrelation functions of each element in .36Na$_2$O•.64SiO$_2$ melt at 2000K.

in also $.36Na_2O–.64SiO_2$ melt. Noted is that the oscillatory features as shown in the velocity autocorrelation for Si and O are also found in these cases, and the periods of oscillations are almost the same. However, long time behaviors of autocorrelation functions is different to each other. The stress autocorrelation function have a long time tail remains up to more than 1ps, and suggests that the characteristic time scale in the stress relaxation is much longer than those of self-diffusion and thermal conduction. The autocorrelation function of energy current behaves differently in the medium time range that a weak oscillation with the period of about 0.2ps is involved. This oscillation is considered to be caused by the motion of sodium atoms since the period is almost the same to that found in the velocity autocorrelation for Na.

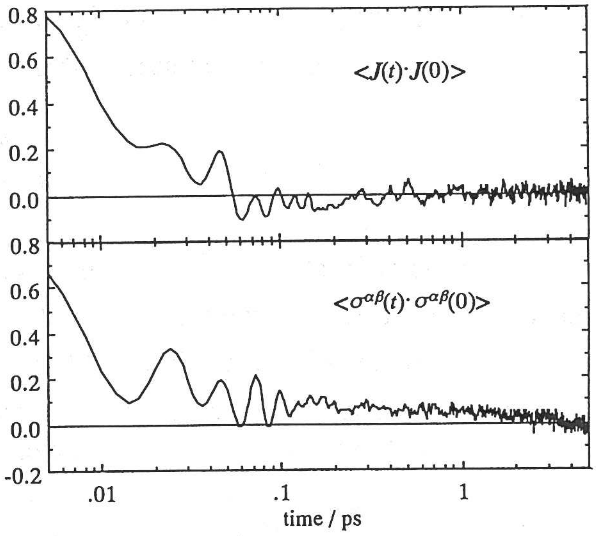

Fig. 2 Normalized autocorrelation functions of shear stress and energy current in $.36Na_2O\cdot.64SiO_2$ melt at 2000K.

The transport properties was calculated from the autocorrelation functions by using eqs. (1-3). The compositional dependence of the simulated self-diffusivity is shown in fig. 3 as a comparison with the experimental data 10]. The present simulation is successful in reproducing the general feature of the compositional dependence of self-diffusivity. The sodium is the most successful one among the constitutional elements for simulating the experimental data.

The result on the shear viscosity is shown in fig. 4 also in comparison with the experimental data [11]. The simulation failed to reproduce a systematic compositional dependence of shear viscosity, and the absolute values seem to be too small compared with the experimental ones. The result on the thermal conductivity is given in fig. 5, and in this case, simulated values show a monotonous increase with increasing the content of Na_2O which is consistent with the experimental result of Ohta *et al.* [12] Unfortunately, the experimental values of thermal conductivity in this system [12,13] are not so well converged, and it is difficult to decide which result is the most reliable one at the present time.

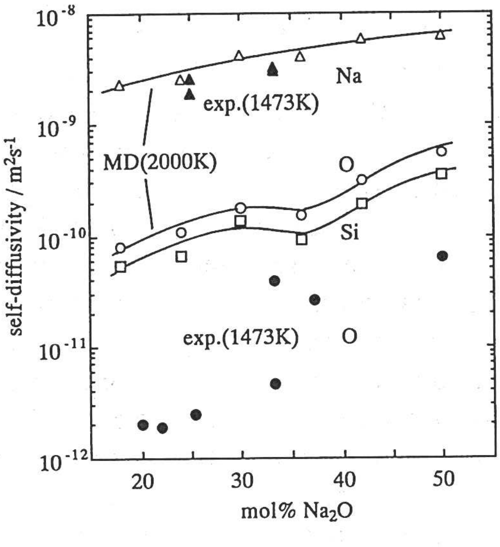

Fig. 3 Compositional dependencies of self-diffusivity of each element in Na_2O-SiO_2 system as comparisons with the experimental values [10].

4. Discussion

As shown above, the applicability of

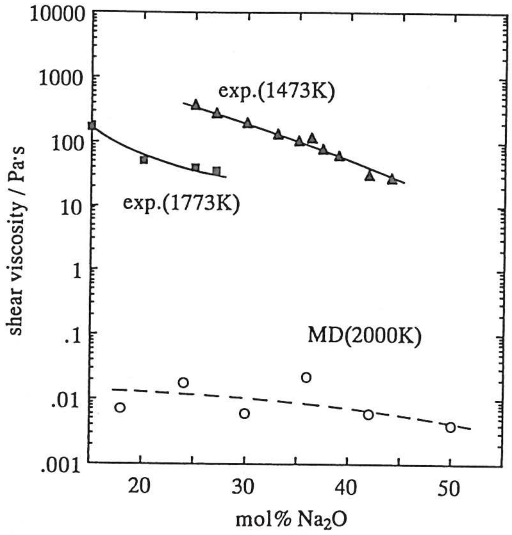

Fig. 4 Compositional dependence of the shear viscosity in Na_2O-SiO_2 system as comparisons with the experimental values [11].

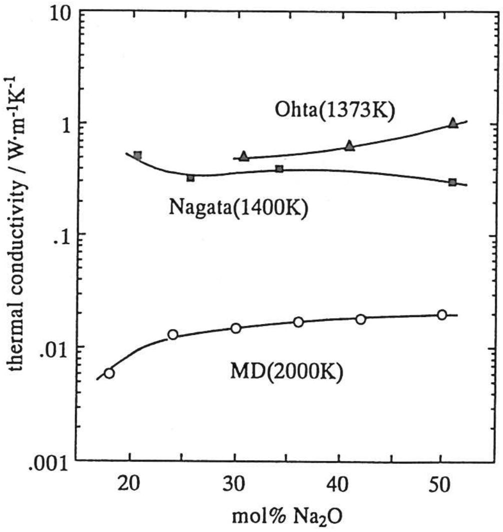

Fig. 5 Compositional dependence of the thermal conductivity in Na_2O-SiO_2 system as comparisons with the experimental values [12,13].

the MD simulation strongly depend on the property which we want to calculate. The order of transport properties in the applicability should be something like: 1) self-diffusivity of Na, 2) self-diffusivities of Si and O, 3) thermal conductivity, and 4) shear viscosity as the worst. We consider the reason for such difference in the applicability as follows.

Since the total momentum of atoms in the basic cell is preserved to be zero, cooperative motion of larger atomic clusters beyond the cell size cannot be reproduced in the MD simulation. The maximum size for cooperative motion is limited to be about the half of the cell size, namely 1.3nm in the present study. And the difference in the applicability to each transport property can be explained by using the limitation of the size of cooperative motion, that is, relatively small area is enough to make a diffusive motion of Na atoms, but a larger space is required for Si and O atoms because their diffusive motions can be achieved only by changing in the network topology. In the simulation of shear viscosity, required size of the cooperative motion in the shear flow [14] possibly exceeds the cell size in the present study.

The other reason for the difference in the applicability is the scale of the correlation time for each transport property. The relaxation time of the shear stress in viscous liquid [14] is considered to be long compared with the time scale in MD simulation (~10^{-10}second), and the relaxation phenomena concerning to $<\sigma^{\alpha\beta}(t)\cdot\sigma^{\alpha\beta}(0)>$ in fig. 2 possibly indicate only a part of whole relaxation phenomena in the shear flow. In the case of thermal conductivity, the relaxation time is closely related to the lifetime of phonon in the melt which is expected to be approximately in the same order of thermal vibrations which should be within the range of the time scale of MD simulation. The results for each transport properties seem to support above discussion.

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