

APPLICABILITY OF MOLECULAR DYNAMICS TO ANALYSES OF REFINING SLAGS

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Synopsis :

CaO-SiO₂ melts with CaO contents ranging 40 to 60 at.% were simulated by molecular dynamics (MD) at 1873K. The calculated pair distribution functions and general tendency of silicon ion fractions with various number of non-bridging oxygen ions agreed well with experiments reported elsewhere. The calculated diffusion coefficient of every ion as a function of CaO content was also in good agreement with the measured values. These demonstrate the promising applicability of MD to slag analyses.

The melt of 45 at.% CaO-45 at.% SiO₂-10 at.% CaF₂ was also simulated by MD to study the effects of fluorine addition to silicate melt. The hypothesis of the existence of di-fluorine ions in some thermodynamic modeling of slags was not verified due to the lack of appropriateness of the interatomic potentials used in this study.

Key words : computer simulation, molecular dynamics, statistic mechanics, slags, pair distribution function, diffusion coefficient

1. Introduction

In classical MD, interatomic potentials, which are expressed as functions of bond length and bond angles with a little number of parameters, are used to solve the Newton's equation of motion of each molecule (atom or ion). These parameters are often assessed by the use of properties, which are already obtained, such as cohesion energy, elastic modulus and the nearest neighbour distance between atoms. Sometimes they are assessed based on energy calculation by the use of molecular orbital method. Since the property values estimated by MD depend on interatomic potentials used, it is necessary to use appropriate potentials in order to estimate reliable property values.

A number of properties can be estimated by a single run of MD as listed in Table 1 [1]. If the form of interatomic potential is chosen properly and the parameters appeared in the potential

Table 1. Material's properties which can be calculated by molecular dynamics simulation.

Structural properties	Thermodynamic properties	Dynamical properties
Pair distribution function Structure factor	Equation of state data Isobaric thermal expansion coefficient Enthalpy Specific heat at constant pressure Specific heat at constant volume Isothermal compressibility	Velocity autocorrelation function Power spectrum
Transport properties	Microscopic information of the atomic distribution	Optical properties*
Diffusion constant Shear viscosity Electric conductivity* Thermal conductivity*	Distribution of volumes of Voronoi polyhedra Distribution of shape parameters of Voronoi polyhedra Distribution of selected of Volonoi polyhedra	RAMAN scattering BRILLOUIN scattering Neutron inelastic scatteving

functions can be assessed or verified in comparisons between calculated and observed values of some properties which are rather easy to be measured, other properties which are rather difficult to be measured can confidently be estimated by MD. The properties listed in Table 1 seem to have little relation with each other at the first glance, but they are deeply correlated through the motion

of molecules and the correlation can be clarified by MD. Therefore, the authors would like to utilize this correlation to estimate properties or cross-check the measured properties from the viewpoint of selfconsistency.

Although more sophisticated MD such as MD with embedded atom method [2] and ab initio MD linked with local density functional theory [3] can be applied to study of slag's properties in the near future, the applicability of molecular dynamics is studied in this work within the region of classical MD from the above mentioned viewpoint.

2. Simulation method

Calcium silicate melts with CaO content ranging from 40 to 60 mole percents were simulated by MD. A melt of 45 at.% CaO-45 at.% SiO₂-10 at.% CaF₂ was also simulated to study the effect of fluorine ions. The total number of molecules in each simulation was chosen as 525. The number of each kind of molecule for each case studied is listed in Table 2. The interval of time step was 0.4 fs, and a cubic unit cell with 19.827Å in side length was used under periodic boundary condition.

Initial coordinates of each molecule were successively generated by the use of random number. When the chosen location of a molecule was closer to its neighbors than 1.5Å, another location was regenerated. Otherwise the molecule sometimes displaced far beyond the limit of the unit cell. The temperature was controlled to be 3000K for initial 2000 steps, reduced to 1873K during the following 3000 steps and kept at 1873K from 5000 to 10000 step by direct velocity scaling of each molecule. The velocity scaling was removed at 10000 step. The data of molecules' positions and velocities are collected from 15000 step to 35000 step for structural and statistical analyses. Since the system temperature did not increase during the period the system was considered to be at thermal equilibrium. The densities of simulated systems calculated by the mole fractions and the volume of the unit cell was close to the observed densities at 1973K [4]

Table 2 Chemical compositions and number of molecules used in molecular dynamics simulation.

case no.	compositions at.%			number of molecules				
	CaO	SiO ₂	CaF ₂	Ca	Si	O	F	total
1	40	60	-	81	121	323	-	525
2	45	55	-	93	113	319	-	525
3	50	50	-	105	105	315	-	525
4	55	45	-	117	97	311	-	525
5	60	40	-	129	89	307	-	525
6	45	45	10	113	93	279	40	525

and the calculated pressure was in the range between 6 and 13 MPa. The following Born-Mayer-Higgins type potential was used for each molecule pair in CaO-SiO₂ system :

$$\phi_{ij} = Z_i \cdot Z_j e^2 / r_{ij} + f_0 (b_i + b_j) \exp \{ (\sigma_i + \sigma_j - r_{ij}) / (b_i + b_j) \} \dots \dots \dots (1)$$

where ϕ_{ij} : interatomic potential and r_{ij} : interatomic distance. The first term in the right hand side is coulomb potential and the second term is inter-core repulsive potential. The parameter values are from Okada et al. [5] regarding SiO₂, and for the potential of Ca-O the values were assessed by the use of the Handbook of Interatomic Potentials issued by Harwell Laboratory. [6] For Ca-F, the following was used referring the same handbook :

$$\phi_{ij} = Z_i Z_j e^2 / r_{ij} + A \exp (-r_{ij} / \zeta) - c / r_{ij}^6 \dots \dots \dots (2)$$

For Si-F and F-O pairs the following function used by Hirao et al.[7] was also utilized in this study :

$$F(r_{ij}) = (q_i \cdot q_j / r_{ij}^2) [1 + \text{sign}(q_i \cdot q_j) \{ (\sigma_i^* + \sigma_j^*) / r_{ij} \}^n] \dots \dots \dots (3)$$

where $F(r_{ij})$: interatomic force.

3. Calculated results

3.1 Structure of melts

Pair distribution function g for every ion pair was calculated from $r=0$ to $r=L/2$. The calculated functions are shown in Fig's. 1 for cases 3. In case 3, the calculated locations of the first peak of Si - Si, O - O, Si - O and Ca - O pair distribution functions agrees well with their nearest neighbour distances observed by Waseda et.al. with X - ray diffraction [8].

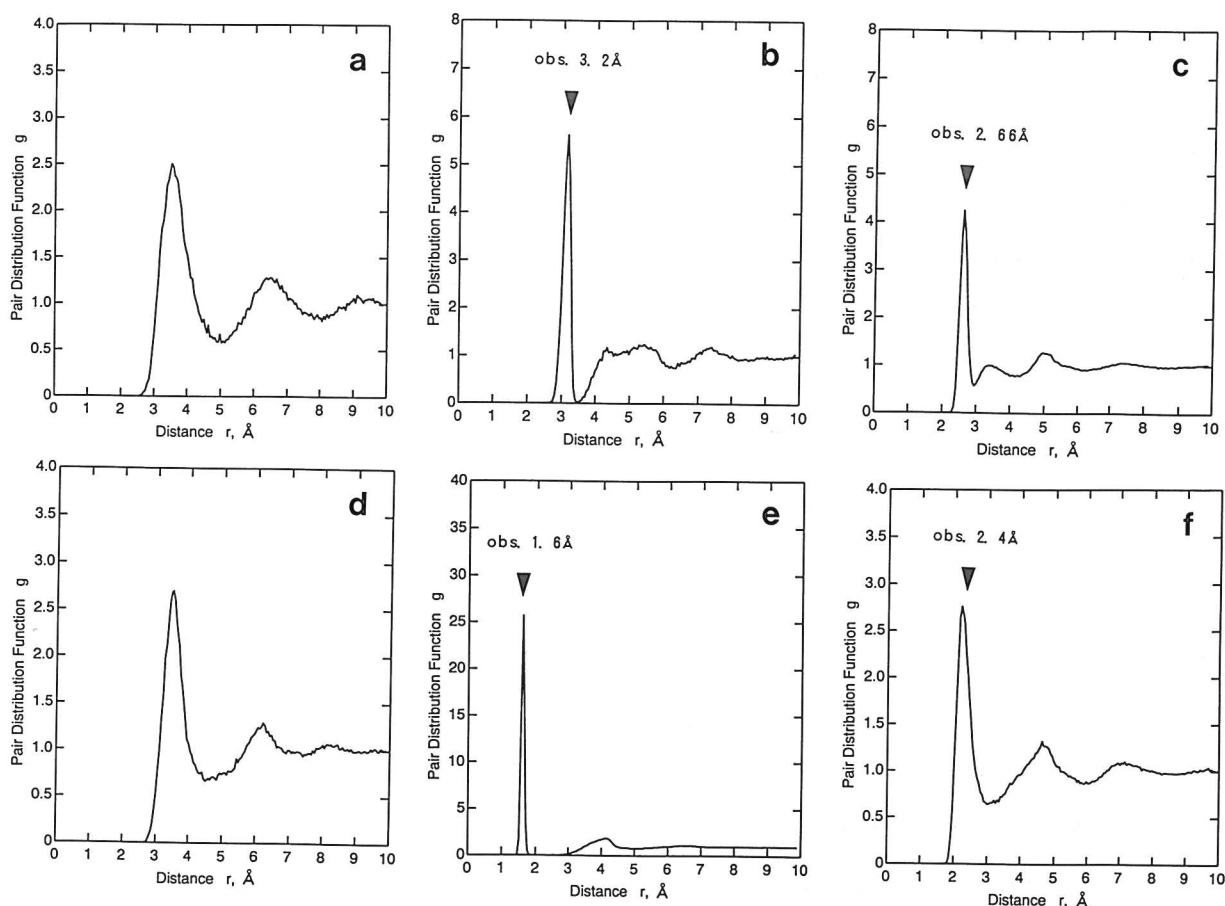


Fig. 1. Calculated pair distribution functions for (a) Ca-Ca, (b) Si-Si, (c) O-O, (d) Ca-Si (e) Si-O and (f) Ca-O pairs for 50at.% CaO-50at.% SiO₂ melt. Solid triangles show the nearest neighbour distance for each pair observed by Waseda et. al. [8]

The number of oxygen ions surrounding a silicon ion was also calculated as a function of the distance r from the silicon ion. The number reaches 4 at a little less than 1.8 Å in cases 1 through 5 as shown in Fig. 2 for case 3 as an example. Each oxygen ion was classified by the number of silicon ions which surrounded the oxygen ion within the distance of 1.8 Å. If the number of silicon ions was two, the oxygen ion was considered as a bridging oxygen. If the number was less than two, the oxygen ion was considered as a non-bridging oxygen. Then, the numbers of silicon ions with various number of non-bridging oxygen ions were calculated. One hundred of time sections with the same interval of 100 time steps were averaged. The calculated results are shown in Fig. 3. The figure shows that the numbers of silicon ions with one and zero non-bridging oxygen decrease as CaO fraction increase, while the numbers of silicon ions with more than two non-bridging oxygens increase.

Pair distribution functions for case 6 was also calculated, but, any conspicuous difference is not observed. The number of each kind of ion surrounding a fluorine ion was calculated as a function of the distance from the fluorine ion for case 6. It indicated that the number of Ca or O reaches one before the number of F reaches one.

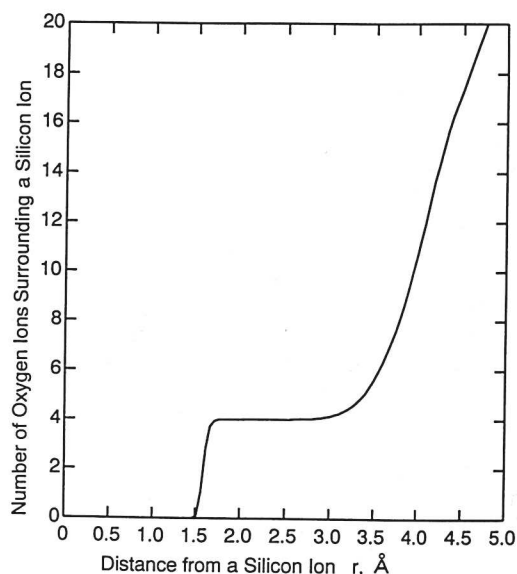


Fig. 2 Calculated number of oxygen ions surrounding a silicon ion as a function of the distance from the silicon ion for case 3.

3.2 Calculated diffusion coefficients

By the use of the following statistical correlation, diffusion coefficients of Ca, Si and O ions in CaO - SiO₂ melts can be calculated :

$$6 D_i \cdot t = x_i^2 \dots\dots\dots (4)$$

where, D_i : diffusion coefficient of molecule i , t : simulated time, and x_i : displacement of molecule i in the simulated time. From the slopes of the plots x_i^2 vs. t , which are shown in appendix A, D_i 's were obtained. The results are summarized in Fig. 4. Generally speaking, the calculated diffusion coefficients increase as CaO fraction increase in CaO - SiO₂ melts at 1873K.

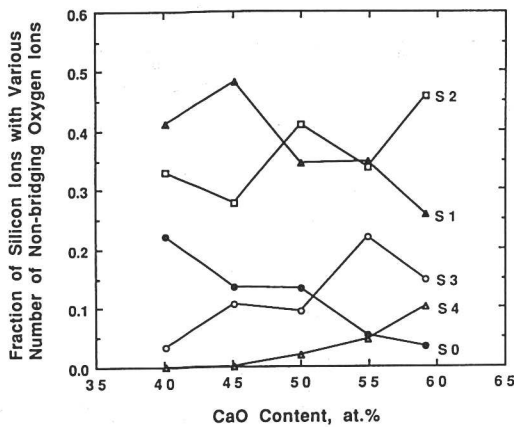


Fig. 3 Calculated fractions of silicon ions with various number of non-bridging oxygen ions as functions of CaO content in CaO-SiO₂ melts.

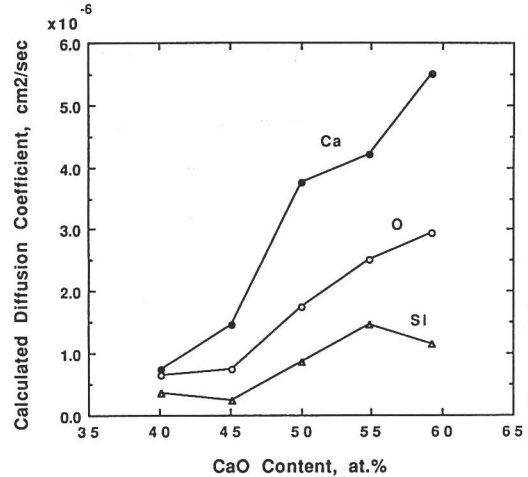


Fig. 4. Calculated diffusion coefficients of Ca, Si and O ions in CaO-SiO₂ melts as functions of CaO content at 1873K

4. Discussion

4.1 Comparison of calculated structure with observations

The agreements between the calculated locations of the first peak in pair distribution functions and the observed nearest neighbour distance are considered to be natural since the empirical interatomic potential used in the present simulations are assessed by the use of the observed nearest neighbour distances.

Kasio et. al. experimentally studied the structure of CaO - SiO₂ at 1873K by Raman spectroscopy, and they measured the fractions of silicon ions with various numbers of non-bonding oxygen ions.[9] Their results are shown in Fig. 5, which can be compared with Fig. 3. They agrees with each other in the general tendency that the fractions of silicon ions with two or four non-bonding oxygen ions (S₂, S₄) increase while the fraction of silicon ions with one non-bonding oxygen ion (S₁) decrease as CaO contents in CaO - SiO₂ melts increase. However, S₂ reaches its maximum at 50 at.% CaO in the observation, but it is not found in the calculated results. The calculated fractions of each kind of silicon ions distributed more evenly than observation where only one or two kinds of silicon ions predominate depending on the CaO content. It means that energetic preference is predominant in observed results and entropical preference is also predominant in calculated results. It is considered to be due to two-body potential approximation in MD. It is also not clear in the experiment the existence of silicon ions with zero and three non-bonding oxygen ions and their effects on Raman spectroscopy, for further comparison with the present calculation.

The author et. al. are developing a thermodynamic model of refining slags based on cell model[10], where the fluorine ions are considered to form doubly charged di-fluorine ions. As far as the present simulation, this hypothesis is not appropriate. However, the authors think the interatomic potentials used in the present study are not suitable enough to conclude it. For this purpose either the potential which considers the effects of electron density distribution for bonding as mentioned before or the potential which considers the effects of the geometric arrangements of every molecules, such as Tersoff - type potential [11] should be utilized.

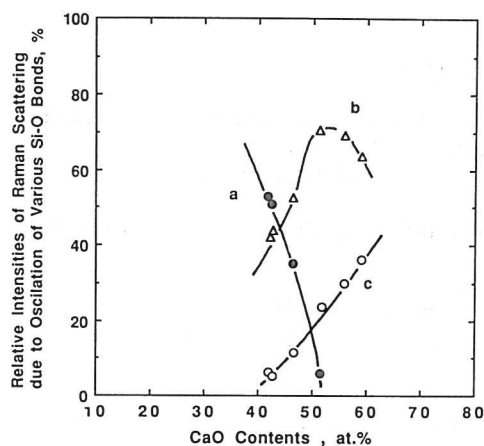


Fig. 5. Intensity of Raman scattering due to stretching and contraction of Si-O bonds in CaO-SiO₂ melts [9]. Curves A, B and C correspond to Si-O bonds where Si ion has one, two and four non-bridging oxygen ions, respectively.

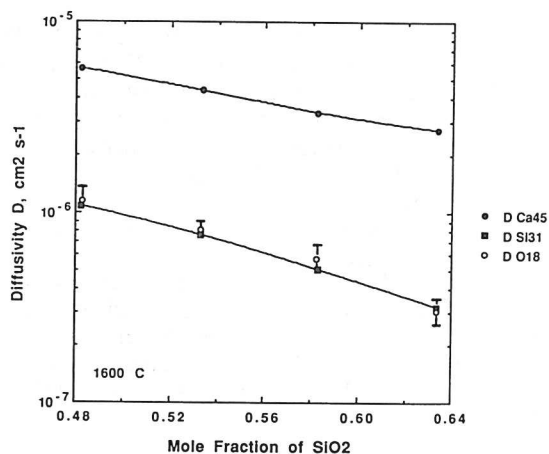


Fig. 6 Measured diffusion coefficients of Ca, Si and O ions in CaO-SiO₂ melts as functions of CaO content at 1873K (after Keller et. al. [12]).

4.2 Comparison of calculated diffusion coefficients with measures ones

Keller et. al. measured the diffusion coefficients of Ca, Si and O ions in CaO - SiO₂ melts. [12] Their reported values at 1873K are shown in Fig. 6. The calculated results (Fig. 4) are quite in good agreement both in the order of magnitude and in the concentration dependency. These agreements are rather astonishing. The authors also tried to calculate viscosity and thermal conductivity of the melts by the use of the same simulated data. However, it was found that it needs two orders of longer simulation time to obtain them based on statistic correlation in atomic motions in equilibrium MD.

5. Conclusions

By the use of Born - Mayer - Higgins type two body potentials, CaO - SiO₂ melts were simulated by molecular dynamics with CaO concentration ranging from 40 at.% to 60 at.% at 1873K. Pair distribution function for every ion pair, fractions of silicon ions with various number of non-bridging oxygen ions and diffusion coefficient of every ion in the melts were calculated. The locations of the first peaks in the calculated pair distribution functions of Ca - O, Si - O, Si - Si and O - O pairs agreed well with the observed nearest neighbour distances for the pairs. The general tendency of the calculated fractions of silicon ions with various number of non-bridging oxygen as functions of compositions agreed well with the observation reported elsewhere in that fraction of silicon ion with a non-bridging oxygen ion decreases while those with two or four non-bridging oxygen ions increase as CaO contents increase. However, some discrepancy was resulted in details between the calculated and observed fractions. The calculated diffusion coefficients were in good agreements with measurements in both the aspects of the order of the absolute magnitude and the their dependency on CaO concentration.

In order to study the effects of fluorine addition, especially on the structure of the melts, 45at.%CaO - 45at.%SiO₂ - 10at.%CaF₂ was also molecular-dynamically simulated. The possibility of the existence of di-fluorine ion in the melts could not be clarified within the limit of the presently used interatomic potentials.

The authors would like to conclude that the applicability of MD to analyses of refining slags is promising, which was demonstrated in the calculation of diffusion coefficients even within the range of the classical MD. In addition, the utilization of more sophisticated treatments of interatomic potential including ab initio MD, is considered to enlarge the applicability further more.

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Appendix

Figures 7 show the plots of mean square displacements of Ca, Si, O and F ions v.s. elapsed time in simulations for, case 6 in Table 2. After certain time of period, the relation between X_i^2 v.s. t becomes approximately straight line. From the slope of the straight line diffusion coefficients of Ca, Si, O and F ions are calculated.

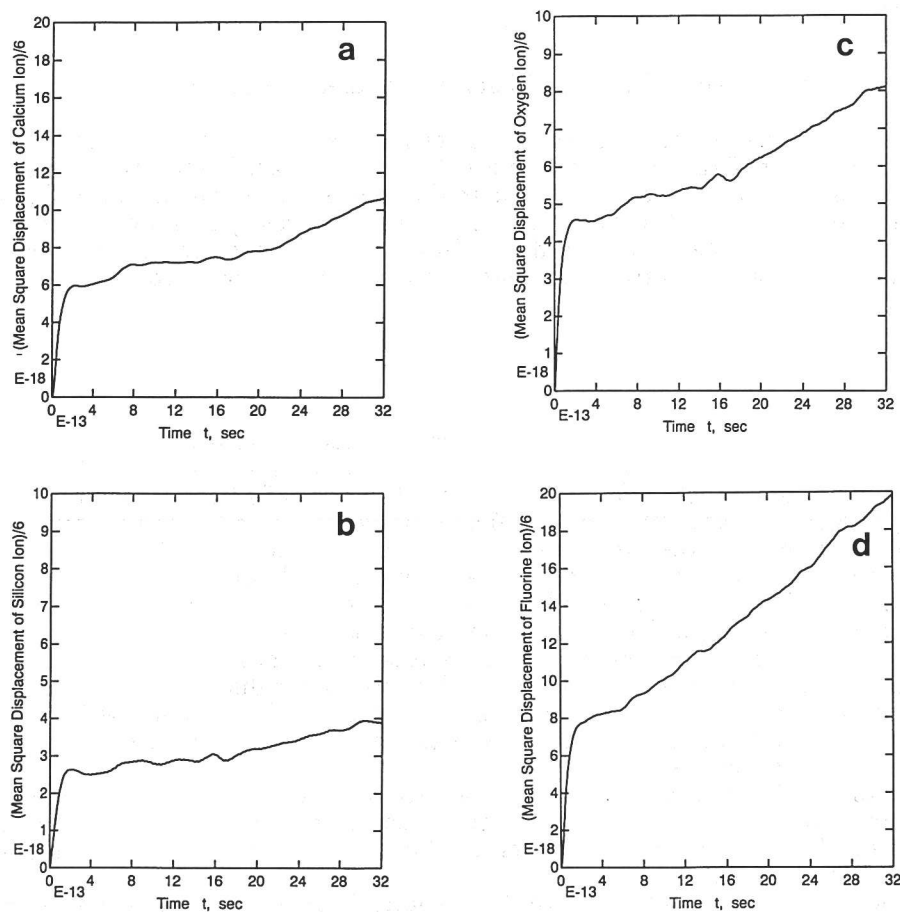


Fig. 7 Plots of the mean square displacements of Ca (a), Si (b), O (c) and F (d) v.s. time elapsed in simulation for case 6]