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# Molecular dynamics of structural properties of molten CaO-SiO<sub>2</sub> with varying composition<sup>①</sup>

WU Yong-quan(吴永全), HUANG Shi-ping(黄世萍), YOU Jing-lin(尤静林),  
JIANG Guo-chang(蒋国昌)

(Shanghai Enhanced Laboratory of Ferro-Metallurgy, Shanghai University, Shanghai 200072, China)

**[Abstract]** Molecular dynamics simulations of the  $x\text{CaO} \cdot (1-x)\text{SiO}_2$  melts ( $x$  varying with the composition of melt) were performed to achieve some structural information. It is found that the first peak positions of Si-Si, Si-O and O-O partial radial distribution functions RDFs (3.165 Å, 1.612 Å and 2.6 Å) agree very well with those of x-ray diffraction experiments. The discovered relation of coordination number  $N_{\text{Si-Si}}(r_0)$  with the molar ratio of CaO is linear and the slope is -0.056 17. The average bond lengths of Si-O<sub>b</sub> and Si-O<sub>nb</sub> are 1.6275~1.630 Å and 1.595~1.60 Å respectively. Both distribution curves of the angles O-Si-O and Si-O-Si show one peak. For the distribution of angle O-Si-O the positions of the peaks are just a little less than the typical tetrahedral angle 109.5°. And for angle Si-O-Si the positions of peaks fluctuate in the range from 148° to 151°. At last, the distribution of five Si-O tetrahedra was obtained and discussed.

**[Key words]** MD simulation, structural properties, CaO-SiO<sub>2</sub> melts

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**[Document code]** A

## 1 INTRODUCTION

The study of molten structure of CaO-SiO<sub>2</sub>, which act as the basic factor influencing the physical and chemical properties of the silicate melts, has great importance in many fields, as metallurgy, mineralogy, geophysics, geology, and amorphous physics. For instance, the fluidity of metallurgical slag is mainly determined by the local structural units. In the latest decades, a number of techniques<sup>[1~5]</sup> were devoted to gain the structural information of molten silicates. One of such methods is molecular dynamics simulation (MD), which has become a valuable tool for achieving insight into the structure of melts at the atomic level. The crucial factor in MD is the selection of a proper inter-atomic potential in order to represent the internal forces acting on the atoms<sup>[1]</sup>. Then the simulation may go further to indicate the structural and chemophysical properties of melts. As a generally accepted conception<sup>[2~9]</sup>, five Si-O tetrahedrons:  $Q_0$ ,  $Q_1$ ,  $Q_2$ ,  $Q_3$ , and  $Q_4$  corresponding respectively to none, one, two, three and four bridging oxygen in one tetrahedral unit are considered to be the basic local structural units. All of silicate melts are composed of these five tetrahedrons but in different proportion and intrinsic chemical potential.

In this paper, molecular dynamics simulations are performed to study the structural change, including RDFs  $g_{ij}(r)$ , coordination numbers  $N_{ij}(r)$ , bond angles of O-Si-O and Si-O-Si and so on, brought about by

increasing CaO fraction in the binary CaO-SiO<sub>2</sub> melts.

## 2 SIMULATION METHOD

During the molecular dynamics simulations of CaO-SiO<sub>2</sub> melts, a type of pair potential of Born-Mayer-Higgins form was quoted<sup>[4]</sup>:

$$u(r_{ij}) = q_i q_j / r_{ij} + B_{ij} \exp(-r_{ij} / \rho_{ij}) \quad (1)$$

where  $u(r_{ij})$  is the interatomic pair potential and  $r_{ij}$  denotes the interatomic distance. The first term in the right hand side represents Coulomb repulsion interaction and the second term represents inter-core short-range repulsion interaction. The parameter values adopted for  $B_{ij}$ , and  $\rho_{ij}$  have been discussed carefully elsewhere<sup>[4]</sup> and here only listed in the Table 1. The ionic valences  $q_i$  for Si, O, and Ca are +4, -2, and +2 respectively.

**Table 1** Parameters for BMH potential

| $ij$  | $\rho_{ij}/\text{\AA}$ | $B_{ij}/\text{eV}$       |
|-------|------------------------|--------------------------|
| Si-Si | 0.025                  | $1.86602 \times 10^{19}$ |
| Si-O  | 0.142 5                | 223 440.54               |
| Si-Ca | 0.222 6                | 1 362.401                |
| O-Ca  | 0.340 1                | 1 179.225                |
| Ca-Ca | 0.420 2                | 247.559                  |
| O-O   | 0.260                  | 15 812.842               |

In each simulation process, 630 atoms were included, and the initial construction is a random configuration that is most benefitting for the simulation of melts and

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liquids. The model box lengths were changed slightly according to the proportion of CaO under the periodic boundary condition. The initial temperature is fixed at 6 000 K for 2 000 steps to mix the system completely. Then equilibration calculation is started and persisted for 5 000 steps to reach the required temperature of 2 000 K. Following equilibration calculation, the system is relaxed for 5 000 steps to discover the RDFs and correlation functions. So the total step number is 12 000, and the time step is 0. 001 ps. As mentioned in previous section, the aim of this paper is to detect the structural change caused by increasing CaO fraction in the binary melt. So the numbers of Si, O, and Ca and the macro-compositions of melt would vary under the condition that the total atom numbers be fixed around 630. The atom numbers and the compositions are listed in Table 2.

### 3 RESULTS AND ANALYSES

#### 3.1 RDFs and coordination numbers

Partial radial distribution functions(RDFs)  $g_{ij}(r)$  is defined as the following equations for homogeneous and heterogeneous pairs:

$$g_{ii}(r) = \{ n_{ii}(r, r + \Delta r) / (4\pi r^2 \cdot \Delta r) \} / \{ N_i(N_i - 1) / 2L^3 \} \quad (2)$$

$$g_{ij}(r) = \{ n_{ij}(r, r + \Delta r) / (4\pi r^2 \cdot \Delta r) \} / \{ N_i N_j / L^3 \} \quad (3)$$

where  $n_{ij}(r, r + \Delta r)$  is the number of  $ij$  atom pairs

with  $ij$  atom distance in the range  $(r, r + \Delta r)$ ;  $N_i$  and  $N_j$  are the numbers of atom  $i$  and  $j$  in the unit box, respectively and  $L$  denotes the side length of the unit box. The simulation results are shown in Fig. 1. The positions of the first peaks of  $g_{Si-Si}(r)$ ,  $g_{Si-O}(r)$  and  $g_{O-O}(r)$  (3. 165 Å 1. 612 Å and 2. 6 Å), which represent the average distances of corresponding two atoms, agree well with the nearest neighboring distances observed by Waseda et al with x-ray diffraction<sup>[6]</sup> (3. 2 Å 1. 6 Å and 2. 66 Å) and that calculated by Belashchenko et al<sup>[8]</sup> (3. 26 Å 1. 63 Å and 2. 65 Å).

**Table 2** Numbers of atoms and composition of melts

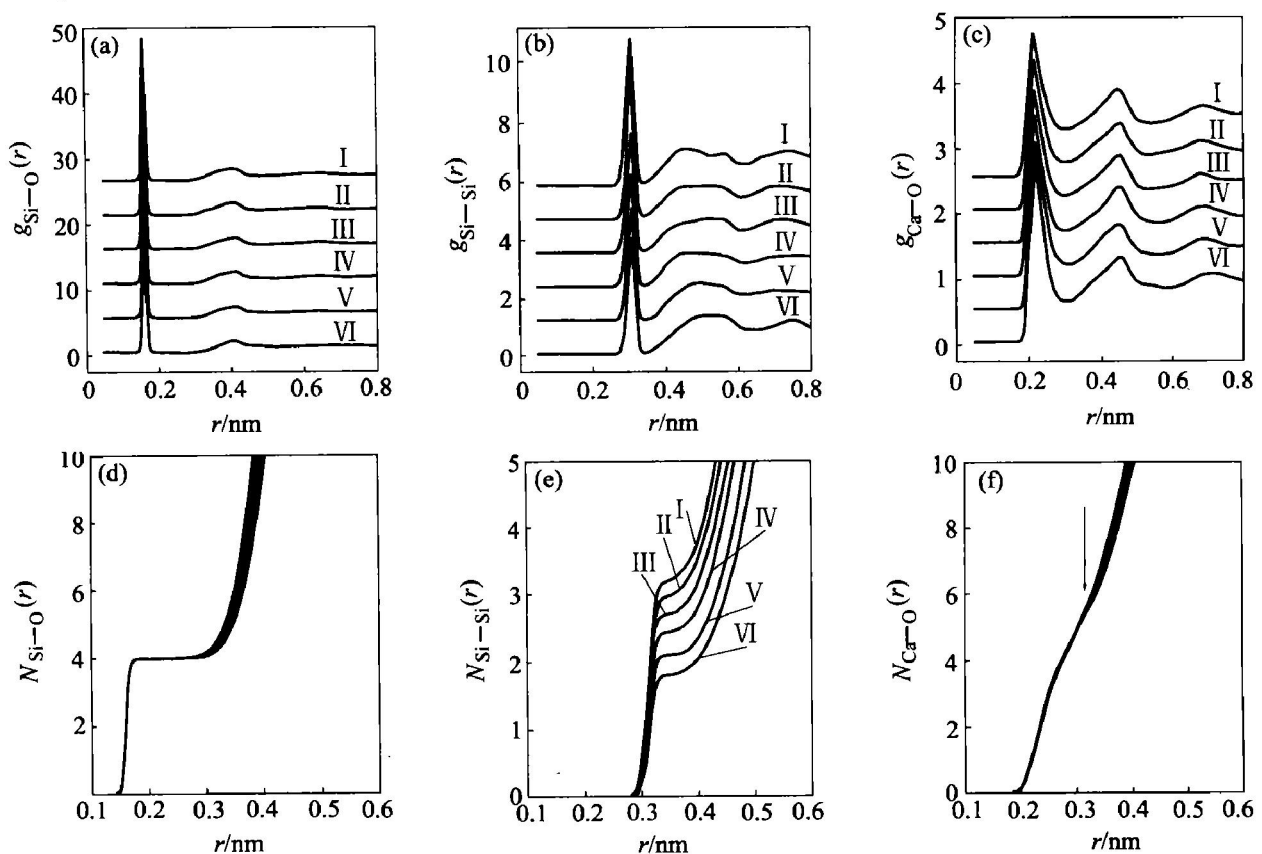
| Sample | $x(\text{CaO}) / \%$ * | Ca  | Si  | O   |
|--------|------------------------|-----|-----|-----|
| I      | 30                     | 70  | 163 | 396 |
| II     | 35                     | 83  | 155 | 393 |
| III    | 40                     | 97  | 145 | 387 |
| IV     | 45                     | 111 | 136 | 383 |
| V      | 50                     | 126 | 126 | 378 |
| VI     | 55                     | 141 | 116 | 373 |

\* —According to phase diagram<sup>[6]</sup>, liquid region at 2 000 K is from 27% to 57% of CaO(mole fraction).

Fig. 1 also shows the results of coordination numbers from the equation as

$$N_{ij}(r) = 4\pi x_j \int_0^r g_{ij}(r') r'^2 dr' \quad (4)$$

According to Fig. 1, the positions of the first



**Fig. 1** Radial distribution function  $g_{ij}(r)$  and coordination number  $N_{ij}(r)$  for various compositions

$g_{\text{Si-O}}(r)$  peaks are fixed at 1.612 Å and they are quite sharp peaks indeed, and almost no change to follow with the variation of CaO content in the melt. On the other hand, the peaks of  $g_{\text{Ca-O}}(r)$  looks quite wide. They cover the range from smaller than 0.2 nm to larger than 0.3 nm. The coordinate number function  $N_{\text{Si-O}}(r)$  displays an uniform platform fixed at 4 corresponding to  $x$ -axis value from 0.17 nm to 0.28 nm. From physical meaning of RDFs, in the radial range of 0.15~0.17 nm there are four oxygen around Si, which implies the typical Si-O tetrahedron. But for  $N_{\text{Ca-O}}(r_0)$  as the arrow shown in  $N_{\text{Ca-O}}(r)$  in Fig. 1(f), the  $y$ -axis value is about 5.65, a bit smaller than 6, which is universally accepted as the coordination number of network modifier<sup>[10]</sup>. The facts mentioned above prove that the Si-O tetrahedra including some  $\text{Ca}^{2+}$  cations are the main local structural map. An instant snapshot of the Sample. (IV) is displayed in Fig. 2.

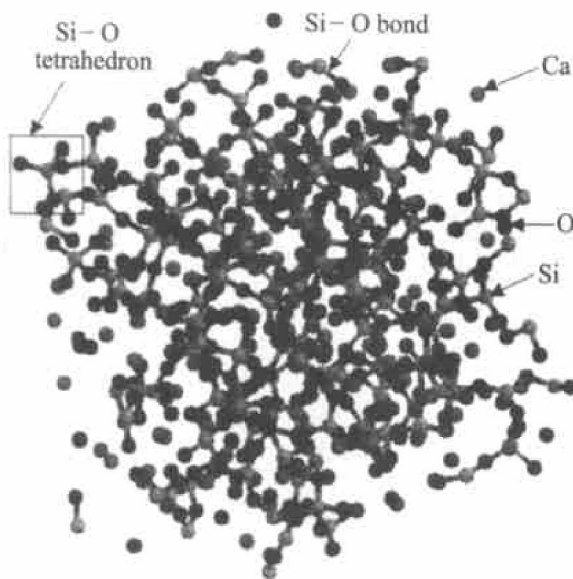


Fig. 2 Instant snapshot of Sample( IV)

The coordinate number  $N_{\text{Si-Si}}(r_0)$ ,  $r_0$  denotes the position of first mini of the curve  $g_{\text{Si-Si}}(r)$ , digitizes the polymerization degree of the melt. As shown in Fig. 3 it linearly varies pursuant to the content of CaO. Because ion  $\text{Ca}^{2+}$  plays as network modifier in the melt, the more the content of CaO, the lower the polymerization degree, and farther the distance between two  $\text{Si}^{4+}$ . If microstructure of the melts goes by the stoichiometry for completely ideal state, which means that all of  $\text{Si}^{4+}$  in melts are network former and all  $\text{Ca}^{2+}$  are network modifier, the slope of the curve in Fig. 3 should be  $-0.06$ . The value of the simulation result,  $-0.05617$ , is very close to the ideal value. So, conclusion can be reached that the structural distribution of calcium silicate melts follows stoichiometry comparatively firmly.

### 3.2 Relative amount of bridging oxygen, non-bridging oxygen and free oxygen

The relative amount of three different oxygen anions were calculated from 100 snapshots of equilibrated phases (one snapshot after an interval of 50 steps in the last 5 000 steps) and the cutoff distance is set to 2.0 Å (within the distance, pair of Si and O can be regarded bonded). The distance was selected according to the platform of the  $N_{\text{Si-O}}(r)$  curve, which corresponds to the first valley of  $g_{\text{Si-O}}(r)$  (within the valley,  $g_{\text{Si-O}}(r) = 0$ , which means that departed from any  $\text{Si}^{4+}$  there is no oxygen existed within the radial range from about 1.7 to 2.6 Å).

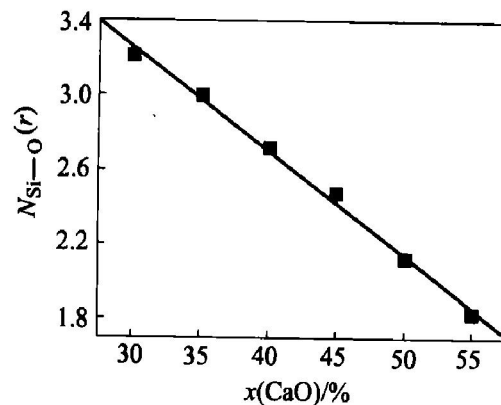


Fig. 3 Coordinate number  $N_{\text{Si-Si}}(r_0)$  varying with molar ratio of CaO

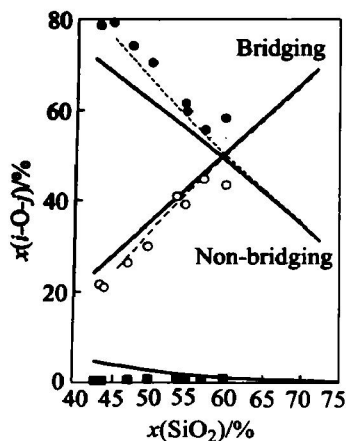
Fig. 4 exhibits the simulation results of the relative amount of three different oxygen anions and the Raman experimental results of TSIMAWALI<sup>[5]</sup>. From comparison, the difference of simulation results and that of experiment is limited to 5%. Moreover, up to 5% free oxygen  $\text{O}^{2-}$  exists in the simulation results, but this concentration is undetectable in the experiment. If neglecting the existence of  $\text{O}^{2-}$ , the content of bridging oxygen  $\text{O}_b(\gamma_1)$  and non-bridging oxygen  $\text{O}_{\text{nb}}(\gamma_2)$  can be expressed as:

$$\gamma_2 = 2x / (2 - x) \quad (5)$$

$$\gamma_1 = (2 - 3x) / (2 - x) \quad (6)$$

where  $x$  denotes the mole fraction of CaO in the melt. This is called ideal state as dash line shown in Fig. 4. Sprenger et al<sup>[11]</sup> also proposed this relation. By means of the ESCA (Electron Spectroscopy for Chemical Analysis) technique, Jen et al<sup>[12]</sup> and Bruckner et al<sup>[5]</sup> measured the ratio of bridging oxygen to non-bridging oxygen in alkaline silicate melts and claimed that the ratio was around that indicating by Eqns. (5) and (6) just as shown in Fig. 5. From Fig. 5, not only the experimental data but also the simulated results fit very well with the solid line and support the ratio equation derived from Eqns. (5) and (6).

### 3.3 Average bond length of Si-O<sub>b</sub> and Si-O<sub>nb</sub>

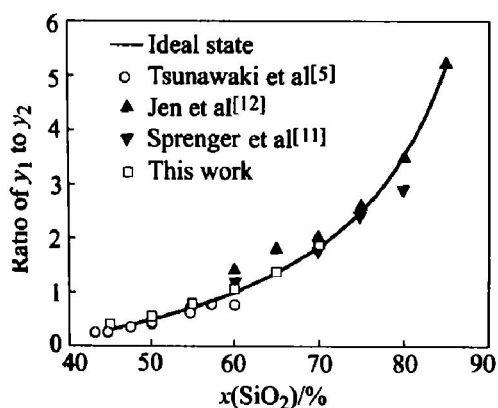


**Fig. 4** Distribution of  $i$ -O- $j$

Solid line—This work, at 2 000 K;

dash line—Ideal state;

Plot—Experimented by Tsunawaki et al<sup>[5]</sup> at 1 600 °C

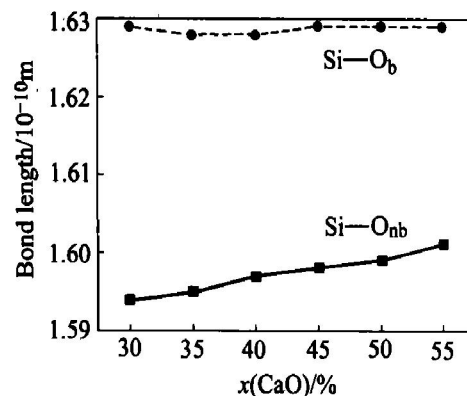


**Fig. 5** Ratio of bridging oxygen to non-bridging oxygen

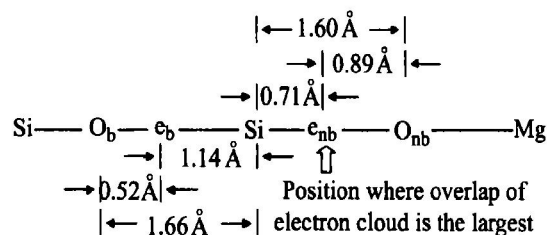
The simulation results of  $d_{\text{Si-O}_b}$  and  $d_{\text{Si-O}_{nb}}$  (the average bond length of  $\text{Si-O}_b$  and  $\text{Si-O}_{nb}$ ) are shown in Fig. 6. As expected,  $d_{\text{Si-O}_b} > d_{\text{Si-O}_{nb}}$  due to that the attraction of  $\text{Ca}^{2+}$  to  $\text{O}_{nb}$  is weaker than that of  $\text{Si}^{4+}$ . Fig. 7 showing the bond situation of magnesium silicate crystal was quoted from F. Liebau<sup>[13]</sup> and interpreted the phenomenon in Fig. 6. It must be noted that the interatomic force has their effect on electron cloud distribution. Following the increase of CaO content,  $d_{\text{Si-O}_{nb}}$  becomes a bit longer from 1.594 Å to 1.601 Å gradually but the length  $d_{\text{Si-O}_b}$  has almost no change. This means that the attraction of  $\text{Si}^{4+}$  or so-called of the local polymeric cluster to  $\text{O}_{nb}$  is gradually weakened, because the local polymeric cluster was broken by  $\text{Ca}^{2+}$  and consequently became smaller.

### 3.4 The Distributions of angles O-Si-O and Si-O-Si

The distributions of bond angles O-Si-O and Si-O-Si are shown in Fig. 8 and Fig. 9, respectively, and were also attained from the selected 100 configurations. Fig. 8(b) is the magnify of the peaks in Fig. 8(a) after

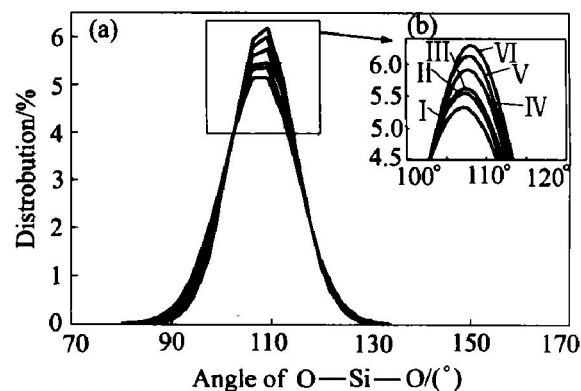


**Fig. 6** Average bond length of  $\text{Si-O}_{nb}$  and  $\text{Si-O}_b$



**Fig. 7** The system of bonds of  $\text{Si-O}_b$ - $\text{Si-O}_{nb}$ -Mg

smoothing transaction. It is clear that the peak of the distribution curves of O-Si-O angle is just beneath 109.5° which is typical for tetrahedral crystal. And the positions of peaks shift to the right side along with the increase of CaO proportion. The distributions of Si-O-Si angles also exhibit peaks as shown in Fig. 9. Linking the tips of these peaks one can get a curve coincides with the fluctuation of  $d_{\text{Si-O}_b}$  shown in Fig. 6. These are possible results, just as the relationship between  $d_{\text{Si-O}_b}$  and angle Si-O-Si suggested by Liebau<sup>[14]</sup> for solid silicate:



**Fig. 8** The distribution of angle O-Si-O

### 3.5 Tetrahedral unit content in melt of different composition

According to the results of high temperature Raman spectroscopy<sup>[14]</sup>, a concept is popularly accepted that various silicate are composed of Si-O tetrahedrons. Gen-

erally, a single crystal of silicate only contains one kind of tetrahedron. But in molten or amorphous silicate, Mysen and McMillan<sup>[2,3]</sup> concluded that there are always several kinds of tetrahedrons coexisted in silicate melts. In fact, many macro-properties of melts such like viscosity are mainly determined by the distribution of Si-O tetrahedrons. Totally, there are 5 kinds of tetrahedrons as shown in Fig. 10 which discovers the content variation of different tetrahedrons versus the increase of CaO molar fraction. By comparing the concentration in terms of  $Q_i$  of alkaline silicate glasses from  $^{29}\text{Si}$  MAS-NMR experiment<sup>[15]</sup> and that of calcium silicate melts of this work shown in Fig. 10, similar trends of each tetrahedron with content of  $\text{SiO}_2$  can be obtained.

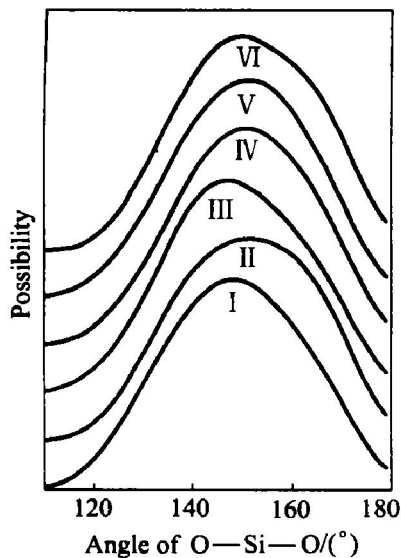


Fig. 9 Distribution of angle Si-O-Si

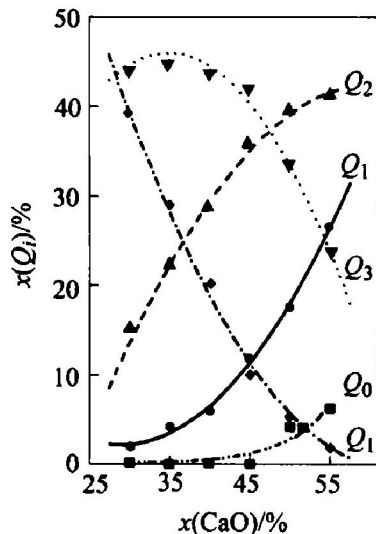


Fig. 10 Distribution of  $Q_i$  versus molar fraction of CaO

As shown in Fig. 10, the curve of  $Q_3$  has a max corresponding to  $x(\text{CaO}) \approx 35\%$  which is lightly higher than the content of crystalline silicate in  $Q_3$ ,  $x(\text{CaO}) = 33.3\%$ . And in any calcium silicate melt there are ex-

actly several kinds of tetrahedrons coexisted. Integrating Fig. 10 with Fig. 4, one can conclude that the microstructure of calcium silicates with any composition are all composed with several kinds of  $Q_i$  units, cation  $\text{Ca}^{2+}$  and minute quantity of free oxygen  $\text{O}^{2-}$ .

## 4 CONCLUSIONS

The structural information of  $\text{CaO-SiO}_2$  melts with various compositions was achieved by means of molecular dynamics simulation (MD). The results agree with those of experiments very well. Based on this investigation, the follow conclusions can be claimed.

1) The characteristics of the peaks of  $g_{\text{Si-O}}(r)$  and  $g_{\text{Ca-O}}(r)$ , as well as  $N_{\text{Si-O}}(r)$  equal to 4 and  $N_{\text{Ca-O}}(r)$  close to 6, indicating that the Si-O tetrahedrons including some  $\text{Ca}^{2+}$  cations are the mainly local structure units.

2)  $N_{\text{Si-Si}}(r_0)$ ,  $r_0$  denotes the position of first mini of the curve  $g_{\text{Si-Si}}(r)$ , digitizes the polymerization degree of the melt. From the slope of the curve of  $N_{\text{Si-Si}}(r_0)$  versus  $x(\text{CaO})$ ,  $-0.05617$ , conclusion can be reached that the structural distribution of calcium silicate melts follows stoichiometry comparatively firmly.

3) Up to 5% free  $\text{O}^{2-}$  can exist in the melts as this simulation pointed out. This concentration is undetectable in the experiment. If neglect the existence of these free  $\text{O}^{2-}$ , then the content of bridging oxygen  $\text{O}_b$  and non-bridging oxygen  $\text{O}_{nb}$  can be expressed as

$$\frac{y_1}{y_2} = \frac{2-3x}{2x}$$

4) Following the increase of CaO content,  $d_{\text{Si-O}_{nb}}$  becomes a bit longer from 1.595 Å to 1.601 Å gradually. But  $d_{\text{Si-O}_b}$  has almost no change. This is because that the polymers in melt become smaller when increasing CaO. So, the abstraction acted by polymer to its non-bridging oxygen becomes weaker.

5) The peak of the distribution curves of angle of O-Si-O is just beneath  $109.5^\circ$  and angle of Si-O-Si is around  $150^\circ$ , and within the range from  $110^\circ$  to  $180^\circ$ .

6) The curve of  $Q_3$  has a max corresponding to  $x(\text{CaO}) \approx 35\%$  which is lightly higher than the content of crystalline silicate in  $Q_3$ ,  $x(\text{CaO}) = 33.3\%$ . The total microstructural units should include several kinds of tetrahedrons,  $\text{Ca}^{2+}$  cations and minute quantity of free oxygen  $\text{O}^{2-}$ .

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