Comparative Study on Molecular Dynamics Simulation Methods of Mechanical Properties of Tricalcium Silicate and Dicalcium Silicate

Yuhuan Bu, Wenxiang Du *

School of petroleum engineering, China University of Petroleum, Qindao, China

*Corresponding author e-mail: wenxiang_du973@163.com

Abstract. A comparative study on the mechanical properties of tricalcium silicate (C$_3$S) and dicalcium silicate (C$_2$S) under different force fields and different sizes by molecular dynamics method. The C$_3$S and C$_2$S single crystal and supercell molecular model were established respectively. The molecular dynamics simulation was carried out under the three force fields of COMPASS, COMPASS II and Universal to obtain the mechanical properties of the nanostructure. It is found that the COMPASS II force field is suitable for C$_3$S and C$_2$S mechanical simulation performance under the same size, which is closer to the literature value. Under the same force field, the large-size unit cell mechanical performance simulation is more stable and reliable than the small-size simulation result. Mechanical properties are one of the most important properties of cement stone. The hydration products of C$_3$S and C$_2$S are responsible for the mechanical strength of the cement stone. Therefore, studying the mechanical properties of C$_3$S and C$_2$S is of great significance for the development of cement materials.

1. Introduction

Cement is the most widely used building material in the world, and Portland cement is the most widely used [1]. With the development of computer technology, molecular dynamics simulation based on classical mechanics is widely used in the fields of biological materials, composite materials, polymers and polymer structures, and is one of the best simulation methods at the nanoscale. This will certainly provide a new perspective for the study of the mechanical properties of cement clinker. There are many components of Portland cement clinker, C$_3$S and C$_2$S are the main bodies, accounting for 50-70% and 15-30% of the total content respectively [2].

C$_3$S consists of three calcium oxides and one silica. The molecular formula is 3CaO·SiO$_2$, also known as Alite. It reacts rapidly with water and is responsible for the formation and development of early strength within 28 days of cement stone. The C$_3$S crystal is composed of independent tetrahedrons, the four corners are Ca$^{2+}$, the center is the oxygen atom, and the P-1 space group. Figure 1(a) shows its single crystal model [3].

C$_2$S is a compound formed by the combination of two calcium oxides and one silica. It is also called belite, and its molecular formula is 2CaO·SiO$_2$. There are many crystal forms such as $\alpha$-C$_2$S, $\beta$-C$_2$S, $\gamma$-C$_2$S. $\beta$-C$_2$S is the most common. It is a P21/N space group, and the silicon tetrahedron and calcium atoms are ordered. $\beta$-C$_2$S molecular model is created in this study. The single crystal is shown in Figure
C₃S hydration rate is slow, which plays a major role in the long-term strength of cement stone after 28d [4].

In molecular dynamics simulations (MD), the choice of force field is critical to the accuracy of the simulated results. Among the many force fields, COMPASS is the first force field based on the ab initio calculation method, which can accurately calculate meteorological properties (structure, conformation, vibration, etc.) and condensed phase properties (condensation energy, etc.), and obtain covalent and non-covalent bonds. Force [5]: COMPASS II force field is developed on the COMPASS force field, can calculate more atom types and types, has a richer functional expression; Universal force field [6] is from the atomic point of view, its calculation range covers the entire periodic table of elements. The mechanical properties of C₃S and C₂S can be simulated in all three force fields, but the adaptability of the model needs to be explored in order to provide basis for subsequent research. The choice of simulated dimensions is equally important for molecular dynamics simulations, given the computational efficiency and accuracy requirements. If the simulation size is too large, more computational resources are required, and the calculation efficiency is low; if the simulation size is too small, the calculation accuracy is difficult to guarantee.

In summary, this study uses a computer for molecular dynamics simulation, which aims to consider the effects of different force field settings, simulation size selection on the mechanical properties of C₃S and C₂S.

2. Simulation part

2.1. Portland cement clinker composition and crystal structure
2.2. Simulation details
Taking the established single crystal cell and super unit cell as the initial structure, the Smart algorithm is first selected to optimize the geometric structure of the atomic structure. This method is the combination of the steepest descent method, the conjugate gradient method and the Newton Lapson method. Then the COMPASS, COMPASS II and Universal force fields were used to carry out molecular dynamics simulation under the NPT ensemble with constant atomic number, pressure and temperature. The whole system adopts Nose pressure control and Berendsen temperature control method, and the temperature and pressure are controlled respectively 298 K and 0.0001 GPa, simulating the room temperature environment; in order to fully relax and ensure the system reaches equilibrium state, the whole simulation duration is set to 100 ps, the time step is set to 0.1 fs, the integral of the motion equation is calculated by Verlet algorithm, Ewald summation method was used to calculate the electrostatic interaction and van der Waals interaction. Finally, the mechanical properties of the equilibrium crystal are calculated. To ensure that the deformation is within the elastic range, the maximum strain amplitude in each direction is set to 0.003. All simulations were performed in the Materials Studio software.

The bulk modulus \( K \) and shear modulus \( G \) of the structure are obtained according to Voigt-Reuss-Hill (VRH) [7] method. The elastic modulus \( E \) and Poisson's ratio \( v \) are solved according to the following equation:
\[ E = \frac{9KG}{G+3K} \]  
\[ \nu = \frac{3K-2G}{6K+2G} \]  

3. Results and discussion

The simulation results are shown in Table 1, Table 2:

| Force field type | Size               | K(GPa) | G(GPa) | E(GPa) | \( \nu \) |
|-----------------|--------------------|--------|--------|--------|---------|
| COMPASS         | single cell        | 46.95  | 25.76  | 65.32  | 0.27    |
|                 | 2a\times2b\times2c supercell | 46.57  | 26.45  | 66.71  | 0.26    |
|                 | 3a\times3b\times3c supercell | 52.45  | 30.28  | 76.18  | 0.25    |
| COMPASS II      | single cell        | 49.68  | 28.00  | 70.71  | 0.26    |
|                 | 2a\times2b\times2c supercell | 49.17  | 27.81  | 70.19  | 0.26    |
|                 | 3a\times3b\times3c supercell | 63.35  | 27.87  | 76.18  | 0.30    |
| Universal       | single cell        | 20.64  | 21.32  | 47.59  | 0.12    |
|                 | 2a\times2b\times2c supercell | 37.81  | 23.49  | 58.38  | 0.24    |
|                 | 3a\times3b\times3c supercell | 42.14  | 23.85  | 60.20  | 0.26    |
|                 | Ref.value [7-8]    | 59.8-84| 25.2-58| 63.3-141| 0.22-0.32|

| Force field type | Size               | K(GPa) | G(GPa) | E(GPa) | \( \nu \) |
|-----------------|--------------------|--------|--------|--------|---------|
| COMPASS         | single cell        | 39.78  | 22.32  | 56.42  | 0.26    |
|                 | 2a\times2b\times2c supercell | 40.01  | 22.73  | 57.34  | 0.26    |
|                 | 3a\times3b\times3c supercell | 42.42  | 25.31  | 63.33  | 0.26    |
| COMPASS II      | single cell        | 36.82  | 24.42  | 60.00  | 0.23    |
|                 | 2a\times2b\times2c supercell | 48.87  | 27.92  | 67.91  | 0.22    |
|                 | 3a\times3b\times3c supercell | 65.94  | 30.85  | 80.06  | 0.29    |
| Universal       | single cell        | 37.09  | 21.09  | 53.19  | 0.26    |
|                 | 2a\times2b\times2c supercell | 35.40  | 20.15  | 50.80  | 0.26    |
|                 | 3a\times3b\times3c supercell | 34.19  | 22.45  | 71.15  | 0.15    |
|                 | Ref.value[9-10]    | 63.2-177| 21.4-116.0| 58-285| 0.19-0.23|

It can be seen from the table that when the simulated size are the same, the bulk modulus and shear modulus calculated by the Universal force field are smaller than those of the COMPASS and COMPASS II force fields, resulting in a significant difference between the elastic modulus and the Poisson's ratio. The Poisson's ratio of C\(_3\)S single crystal is only 46% of the COMPASS II force field calculation, which deviates from the literature value. The Universal force field is not suitable for simulating the mechanical properties of C\(_3\)S and C\(_2\)S. Compared with the literature value, the bulk modulus calculated by the COMPASS force field. The C\(_3\)S and C\(_2\)S bulk modulus values calculated by the COMPASS force field are smaller than the literature values in different size, but more consistent with the literature value when calculated by COMPASS II force field. So the COMPASS II force field is suitable for simulating the mechanical properties of C\(_3\)S and C\(_2\)S.

Under the COMPASS II force field, the bulk modulus of C\(_3\)S and C\(_2\)S single crystal and 2a\times2b\times2c supercell is smaller than the experimental value, but the bulk modulus, shear modulus and elastic modulus of 3a\times3b\times3c supercell are in good agreement with the literature values, indicating that when the simulation size is large, the calculation error caused by accidental error and size effect can be effectively reduced. This result is consistent with the general perception.
4. Conclusion
This study compares the molecular dynamics simulation methods of C$_3$S and C$_2$S and obtains the following conclusions:

(1) Molecular dynamics simulation study the mechanical properties of C$_3$S and C$_2$S are feasible, and the simulation results are in good agreement with literature values.

(2) COMPASS II force field is more suitable for the study of mechanical properties of C$_3$S and C$_2$S. Comparing the simulation results of COMPASS, COMPASS II and Universal force field, the simulation results of the Universal force field are generally smaller than those of the COMPASS and COMPASSII force fields, and the deviation from the literature value is large; The COMPASS compared with COMPASS II force field, COMPASSII force field on the mechanical properties of C$_3$S and C$_2$S simulation is more applicable. It is suitable for studying the mechanical properties of C$_3$S and C$_2$S ionic-covalent bonds.

(3) The mechanical properties of large-size simulation calculations are stable and reliable. The calculation results of bulk modulus, shear modulus and elastic modulus of the 3a×3b×3c supercell model are more stable and reliable. Hence, the large size model can avoid the calculation deviation caused by size effect and accidental error when the calculation resources are allowed.

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