Molecular Dynamic Simulation of Failure of Ettringite

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Abstract. Ettringite is an important component in the hydration products of cement paste. To better understand the failure modes under tensile loading of cement-based materials, mechanical properties of each individual hydration product needs to be evaluated at atomic scale. This paper presents a molecular dynamic (MD) method to characterize and understand the mechanical properties of ettringite and its failure modes. The molecular structure of ettringite is established using ReaxFF force field package in LAMMPS. To characterize the atomic failure modes of cement paste, MD simulations were conducted by applying tensile strain load and shear strain load, respectively. In each MD failure simulation, the stress-strain relationship was plotted to quantify the mechanical properties at atomic scale. Then elastic constants of the ettringite crystal structure were calculated from these stress-strain relationships. MD simulations were validated by comparing the mechanical properties calculated from LAMMPS and those acquired from experiments. Future research should be performed on bridging-relationships of mechanical properties between atomic scale and macroscale to provide insights into further understanding the influence of mechanical properties at atomic scale on the performance of cement-based materials at macroscale.

1. Introduction

Tensile strength is one of the major mechanical properties influencing the initiation and propagation of cracks in cement-based materials. Cracks exhibit more in cement paste with low tensile strength, consequently reducing durability of cement-based materials. Therefore, it is meaningful to understand how the mechanical properties influence the performance of hardened cement paste and other cement-based materials at atomic scale.

There are mainly four types of cement hydrates: calcium silicate hydrate (C-S-H), calcium hydroxide (CH), “alumina, ferric oxide, tri-sulfate” (AFm) and "Alumina, Ferric oxide, mono-sulfate" (AFt) phases (including ettringite, monosulphate, and monocarbonate, etc.). Figure 1 plots the volume percentage of each composition in hydrated Portland cement paste after the hydration of 14 months [1]. Among these cement hydration products, ettringite is a calcium aluminium sulfate mineral crystalizing in the trigonal system with the chemical formula of Ca₆Al₂(SO₄)₃(OH)₁₂·26H₂O. It plays an important role in the crystallization development of cement hydration products and in the deterioration of hardened cement concrete due to sulphate attack [2-4].

This paper conducts series of molecular dynamic (MD) simulations using the ettringite molecular structure in Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS). The mechanical properties of the ettringite molecular structure under strain loadings are investigated in MD simulations with the comparison with experimental results. A detailed understanding of the ettringite...
regarding to mechanical properties and failure modes is helpful for the prediction of crack failures in the long-term performance of hydrated cement concrete at macroscale.

![Figure 1](image-url)

**Figure 1.** Volume percentage of phases in hydrated Portland cement paste, water-cement ratio=0.5, hydrated for 14 months (data are from [1]).

### 2. Computational theory

Ettringite molecular structure is established based on ReaxFF force field in LAMMPS; the optimized parameters are documented in a ffile file with atom positions in a data file from Liu et al.’s work [5]. The ReaxFF force field calculates the atomic interactions in ettringite with good accuracy. The total energy in ReaxFF is partitioned in different energy terms as defined by the following equation.

\[
E_{\text{total}} = E_{\text{bonds}} + E_{\text{angles}} + E_{\text{torsions}} + E_{\text{H-bonds}} + E_{\text{vdW}} + E_{\text{Coulomb}} + E_{\text{lp}} + E_{\text{over}} + E_{\text{under}} + E_{\text{pen}} + E_{\text{coa}} + E_{\text{C2}} + E_{\text{triple}} + E_{\text{conj}}
\]

(1)

where \(E_{\text{bonds}}\) is the sum of all bonded pairwise interactions directly derived from bond orders; \(E_{\text{angles}}, E_{\text{torsions}}, E_{\text{H-bonds}}, E_{\text{vdW}},\) and \(E_{\text{Coulomb}}\) are angle, torsional, hydrogen bond, van der Waal, and Coulomb interactions respectively; \(E_{\text{lp}}\) is the sum of the long pair energy, a penalty for breaking up long pairs in O, N; \(E_{\text{over}}\) is the sum of overcoordination energy, penalty for overcoordinating atoms; \(E_{\text{under}}\) is the undercoordination energy, contribution for the resonance of \(\pi\)-electron between undercoordinating atoms; \(E_{\text{pen}}\) is the penalty for “allene”-type molecules (H=C=C=CH\(_2\)); \(E_{\text{coa}}\) is the energy term due to the contribution of three-body angle conjugation in -NO\(_2\) groups; \(E_{\text{C2}}\) is an energy correction that destabilizes the stability of C=C; \(E_{\text{triple}}\) is a triple bond stabilization energy in CO bonded pairs; \(E_{\text{conj}}\) describes the contribution of conjugation stability to the molecular energy.

A ReaxFF force field was developed for ettringite to simulate the first principles quantum mechanism interaction in hydrous calcium aluminium sulphate systems (H/Ca/Al/S/O) with good accuracy [5]. The geometries and energies of species and complexes in ettringite were calculated according to density functional theory (DFT); ReaxFF parameters were adjusted with the minimum differences between ReaxFF energies and DFT energies. Figure 2 plots a 2×2×1 molecular triclinic supercell structure, a basic calculation structure in the simulation using LAMMPS. The conformity and structure stability of proposed molecular structure using the aforementioned ReaxFF force field parameters were validated in an isothermal-isobaric (NPT) ensemble at room-temperature, and the predicted structures from MD simulations are in close agreements with experiments [5].
3. Result and Discussion

MD simulations of tensile and shear failures of ettringite were performed on periodic boundary condition in three directions under strain loads to characterize the mechanical properties of ettringite. The stress-strain responses under different ambient temperatures were also investigated.

3.1 Elastic Tension failures at atomistic scale

An initial molecular structure of 10×4×4 ettringite supercell structure was adopted in a NPT ensemble at 1 atm of ambient pressure. Temperature was set at 280 K throughout the simulation. Figure 3 plots the uniaxial stress-strain relationship in x-direction of the ettringite molecules. A tensile load was applied at the constant engineering strain rate of 0.001 fs⁻¹. The ensemble was equilibrated by performing an energy minimization of the system with a stopping tolerance for energy of 1×10⁻⁶ Kcal/mole and for force of 1×10⁻⁶ Kcal/mole-Angstrom. Timestep was set as 0.002 fs, and a total of 1000 fs was applied. The deformations of the ettringite molecules in three directions and the stresses of the whole ensemble were documented for each timestep, and the last 400 fs was used for data collection. There was a tensile failure at the tensile strain of 8% along x-direction. According to Liu et al. [5], there is a dramatically decrease of the total number of Ca-O bonds after the tension failure.

Similarly, figure 4 depicts the stress-strain relationship at both compression and tension in x-direction within a very small strain range of ±1%, where positive strain denotes tension and negative strain denotes compression. Figure 5 plots the shear stress-strain relationship under a velocity load of 0.002 Angstrom/ps in x-direction. The molecular structure failed at the shear strain of 1.4%.
Figure 3. Tensile stress-strain relationship along x-direction due to the tensile strain load

Figure 4. Stress-strain relationship due to strain load along the x-direction in the limit of small deformation

Figure 5. Shear stress-strain relationship due to a velocity load in x-direction
Table 1 tabulates the elastic constants of the ettringite crystal. Elastic constants were determined from the stress-strain relationships in LAMMPS simulations within very small strain ranges, where the stress-strain relationship is linear. These calculated elastic constants from LAMMPS simulations are in good agreement with experimental results.

| Elastic constants (GPa) | LAMMPS | Experiment [6] |
|------------------------|--------|----------------|
| $C_{11}$               | 30     | 35.1 ± 0.1     |
| $C_{12}$               | 20.1   | 21.9 ± 0.1     |
| $C_{13}$               | 20     | 20.0 ± 0.5     |
| $C_{14}$               | 1.5    | 0.6 ± 0.2      |
| $C_{33}$               | 52     | 55.0 ± 1.0     |
| $C_{44}$               | 12.2   | 11.0 ± 0.2     |
| $C_{66}$               | 4.9    | 6.6 ± 0.2      |
| Bulk modulus ($K$)     | 25.8   | 27.3 ± 0.9     |
| Shear modulus ($G$)    | 12.2   | 9.5 ± 0.8      |
| Poisson’s ratio ($\nu$)| 0.335  | 0.34 ± 0.02    |

3.2 Stress-strain relationship at different ambient temperatures

Figure 6 plots the tensile stress strain relationships in x-direction under varied temperatures of 1 K, 100 K, and 200 K respectively. As the ambient temperature increases from 1 K to 200 K, the critical stress, when tensile failures occur, decrease from 3.67 GPa down to 2.73 GPa. And the critical strain also shows a similar decrease trend. A possible reason is that atoms with higher kinetic energies at a higher temperature are more likely to break interatomic bonds at smaller deformations. According to the experimental results in [7], the elastic modulus of hydrated Portland cement with a water-cement ratio of 0.33 shows a increase trend, while the ambient temperature increases provided that the temperature is lower than 400 Fahrenheit (477.594 K).

![Figure 6. Tensile stress-strain relationships in x-direction under different ambient temperatures](image)

4. Summary
MD simulations of the ettringite molecular structure were conducted in a NPT ensemble using LAMMPS. Tensile and shear failures were investigated to determine elastic constant from the linear stress-strain relationships at very small strain ranges. The calculated elastic constants showed good agreement with experimental results, which validates the accuracy of the MD simulations. The stress-strain relationship under different ambient temperatures showed that the critical stress and critical strain decreases as the ambient temperature increases. A possible reason is that atoms with greater kinetic energies at a higher temperature are easier to escape from interatomic bonds.

Future research should be conducted on the establishment of corresponding bridging-relationships of mechanical properties between atomic scale and macroscale. These bridging-relationships can provide insights into understanding how the mechanical properties and crack failures at atomic scale influence crack failures of cement paste and other cement-based materials at macroscale.

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