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MOLECULAR DYNAMICS INVESTIGATION OF THE EFFECT OF INTERLAYER CAVITIES OF THE STRUCTURE OF CALCIUM SILICATE HYDRATE AT THE ATOMISTIC SCALE

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Abstract. Calcium silicate hydrate (CSH) gel, as the most important component of hydration products, has the most significant effect on the properties of hardened cement paste. One of the most critical factors affecting the mechanical properties of CSH is the interlayer cavities in the gel. In this study, the effect of these cavities on Young's modulus of CSH has been investigated. For this purpose, first, the atomic structure of CSH is created, and then interlayer cavities with different dimensions are created inside the structure. For modelling, first, a super cell with dimensions of 3 × 6 × 1 times the unit cell of Tobermorite is prepared, and then each of these layers are placed on both sides of the new cell, and a space is created between these two layers. This distance is basically the cavity between the layers. The cavities are made in three sizes of 0.5, 1, and 2 nm, and water is then absorbed by the Grand Canonical Monte Carlo (GCMC) method. Then the created structures are simulated using the molecular dynamics method, and finally, Young's modulus is extracted. The results confirm the effect of the interlayer cavity on reducing the Young's modulus of CSH gel. As the dimensions of the cavity increase, the amount of water absorbed in the cavity increases, leading to a decrease in the Young's modulus of CSH.

1 INTRODUCTION

Concrete is a mixture of cement, water and aggregate that the combination of cement with water leads to a hydration reaction and this chemical reaction produces products whose quantity and quality of products cause different properties in concrete. Any change or defect in hydrated cement paste products can lead to changes in the final properties of concrete, so the use of new methods and technologies to better understand hydrated cement paste products is necessary [1].

The main products of hydration in hardened cement paste are: calcium silicates hydrate (CSH), ettringite, hydrogarnet and monosulfoaluminate. The combination of these products in hardened cement paste leads to the production of a heterogeneous and complex composite whose properties require extensive studies [2]. In recent years, extensive research has been done on hydration products. Due to the laboratory limitations of recognizing the microstructure of cement paste, especially in the nano dimension, the use of simulation methods has received

more attention in recent years [1]. The study of the nanostructure of hydrated cement paste products helps to improve the macro-dimensional properties by examining the defects and nature of the material.

One of the methods for studying materials in the nanoscale and understanding the atomistic structure of materials is the use of molecular dynamics (MD) simulation. The results of studies have shown that MD method is a suitable method for simulating different compounds and has provided favorable mechanical properties results [1]. This method has recently been used in studies related to cement-based products and has had good results.

The most comprehensive study on the use of molecular dynamics of hydration products has been considered in a dissertation by Manzano [3]. In this study, most of the hydration products as well as the cement phases were simulated and its various properties were investigated. Molecular dynamics simulation of Tobermorite 11Å and 14Å has been considered in another study [4]. The results of this study show that the use of MD method for hydration products can be appropriate. Other researchers have studied the properties of some hydrated cement paste products as well as the cement phases with MD method [5-8].

CSH gel as the most important product of hydrated cement paste products, has been considered in this study. One of the issues that can be modelled and simulated using atomistic simulation methods and also has a special importance in the mechanical properties of cement paste is the interlayer cavities in CSH gel that has been investigated in this study. Previous studies have shown that the dimensions of these cavities vary between 0.5 to 10 nm, in which the values of 0.5, 1 and 2 nm have been investigated [9, 10].

2 MODELING AND SIMULATION

The most important hydrated product in cement paste is CSH. This gel is produced by reacting C2S and C3S phases of cement with water. This product makes up about 50 to 70% of the hardened cement paste. Most of the durability, mechanical properties and dimensional stability properties of concrete depend on this product [4]. CSH is almost amorphous and despite modern technologies in the field of material identification, the exact structure and ratio of its constituents have not been determined yet. However, most researchers believe that this gel has a layered structure similar to a mineral called Tobermorite. Tobermorite has silicate chains with calcium atoms between the chains. About 30 different materials with similar structure to CSH have been identified and proposed so far, but research has shown that there is the greatest similarity in structure and properties in Tobermorite. There are four different types of Tobermorite, including 9Å, 11Å, 14Å, and Clinotobormorites. Among these, the most similarity in terms of mechanical properties has been observed in Tobermorite 14 Å [4]. This type of Tobermorite is more hydrated than other verities. Due to the most proven similarity between this material and CSH gel in cement paste products, in this study, this material has been used to investigate the mechanical properties of CSH. Figure 1 shows the crystal structure and Table 1 shows the crystal lattice parameters of Tobermorite 14Å.

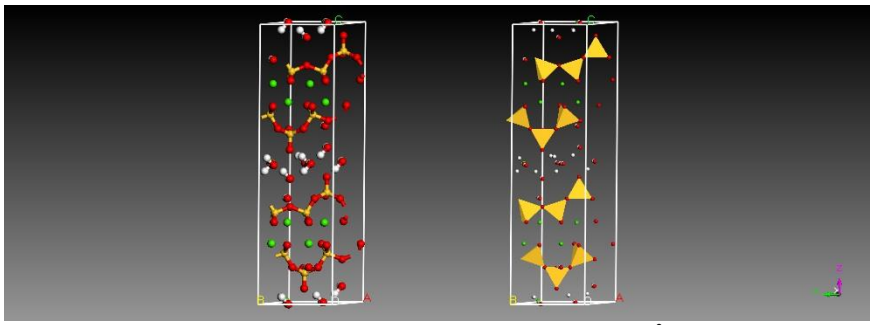

Figure 1: crystal structure of Tobermorite 14Å

Table 1: Crystallographic lattice parameters of Tobermorite 14Å [11].

γ (˚)	β (˚)	α (˚)	c (Å)	b (Å)	a (Å)
123.25	90	90	27.98	7.42	6.73

MD method has been used to simulate atomistic structures. MD method is one of the powerful methods in simulating different materials. Predicting the mechanical properties of materials is one of the capabilities of this method, which is done with good accuracy. The main basis of this method is to solve Newton equations in terms of potential interaction between molecules and external factors. After simulation, different properties of the material can be extracted using statistical mechanical analysis.

One of the most important characteristics in MD is the selection of suitable potential functions and force field. Force fields can cause drastic changes in results. In the field of cement based materials, many force fields have been used. One of the force fields that has been used in some recent studies and a good result has been obtained from it, is the COMPASS force field. According to the list of molecules and interactions presented for this force field, it seems that there is no limit to the use of this force field for Tobermorite. On the other hand, previous results have shown that this force field is suitable for cement based materials [4, 5, 8]. Due to the characteristics of this force field and their use in previous studies, this force field has been utilized in this study.

Before starting the simulation, it is necessary to optimize the structure in terms of dimensions. Optimization of the crystal structure and energy minimization is performed by the Smart method, which is a combination of Newton-Raphson minimization methods, reduction slope method and gradient method. After minimizing the structure, the process of MD simulating is performed on the structures. Periodic boundary conditions are applied to the structures in all three directions. To integrate the MD equations in time, the velocity Verlet algorithm is used. The assumed parameters for simulation are given in Table 2.

After performing MD simulations, the elastic properties of the material are calculated by the elasticity relations. For this purpose, the simulated structures are applied by different strain patterns in different steps and finally 6 × 6 matrices of hardness and softness are obtained. In calculating the elastic properties of materials to ensure linear deformation of materials, the maximum strain is kept in the range of 0.003. Finally, the elastic stiffness coefficient of C_{ijkl} at constant temperature T is related to the stress σ_{ij} and the strain ε_{ij} by Equation (1) [3, 6].

Table 2: Simulation details and parameters.

Parameters	Condition in this work
Ensemble	NPT
Summation method	Ewald
Cut-off distance	12.5Å
Temperature	298 K (Room temperature)
Temperature control (MD)	Nosé thermostat
Pressure	0.0001 GPa (Air pressure)
Pressure control	Berendsen barostat
Dynamic time (MD)	300 ps to 500 ps
Time step (MD)	1 fs
Boundary conditions	Three dimension periodic boundary condition
Maximum strain amplitude in each strain configuration	0.003
Energy minimization process	Smart minimizer method

$$C_{ijkl} = \frac{\partial \sigma_{ij}}{\partial \varepsilon_{kl}}\Big|_{T,\varepsilon_{kl}} = \frac{1}{V_0}\frac{\partial^2 A}{\partial \varepsilon_{ij}\partial \varepsilon_{kl}}\Big|_{T,\varepsilon_{ij},\varepsilon_{kl}} \quad (1)$$

In this relation V_0 is the volume of the crystal lattice in the deformed state and A is the Helmoltz free energy constant.

By calculating the two elastic constants of shear modulus (G) and bulk modulus (K), other elastic properties of the material can also be calculated. To calculate these two values, the approximation methods of Reuss and Vogit have been used. Equations (2) to (5) express the relationship between the stiffness matrix and elastic properties of the material. In these relationships, the R and V indices represent the Reuss and Vogit methods, respectively. S_{ij} also represents the elements of the soft matrix [3, 6].

$$G_V = \frac{1}{15}[C_{11} + C_{22} + C_{33} + 3(C_{44} + C_{55} + C_{66}) - (C_{12} + C_{13} + C_{23})] \quad (2)$$

$$G_R = 15\left[4(S_{11} + S_{22} + S_{33} - S_{12} - S_{13} - S_{23}) + 3(S_{44} + S_{55} + S_{66})\right]^{-1} \quad (3)$$

$$k_V = \frac{1}{9}[C_{11} + C_{33} + 2(C_{12} + C_{13} + C_{23})] \quad (4)$$

$$K_R = [S_{11} + S_{22} + S_{33} + 2(S_{12} + S_{13} + S_{23})]^{-1} \quad (5)$$

Given that the Reuss and Vogit methods report the upper and lower amplitudes of elastic constants, and given the large distance between the two values, the Hill method is proposed to report the mean values of the two numbers. In this study, the final number reported by the approximate, Reuss-Vogit-Hill (VRH) is reported. Relationships (6) and (7) show this approximation [3].

$$K_{VRH} = \frac{K_V + K_R}{2} \quad (6)$$

$$G_{VRH} = \frac{G_V + G_R}{2} \quad (7)$$

After calculating the mean values of shear modulus (G) and bulk modulus of materials, the mean values of modulus of elasticity (E) and Poisson's ratio (ν) are calculated using equations (8) and (9) [3].

$$E = \frac{9G}{3 + G/K} \quad (8)$$

$$\vartheta = \frac{3 - 2\,G/K}{6 + 2\,G/K} \quad (9)$$

In order to model the final samples and the cavities in them, a simple initial model for interlayer cavities was built and the elastic properties of the new models were calculated. First, a cell with dimensions of 3 × 6 × 1 times the size of a single cell is prepared and then each of these layers is placed on both sides of the new cell and a space is created between these two layers of Tobermorite. This distance is basically the desired cavity between the layers. These cavities in cement paste play a major role in properties. The cavities were created in three sizes of 0.5, 1 and 2 nm and then water was absorbed to them by the Monte Carlo (GCMC) method. After preparing the models, molecular dynamics simulations were performed on them and finally the elastic properties were measured. Built-in models are shown in Figures 2 to 4.

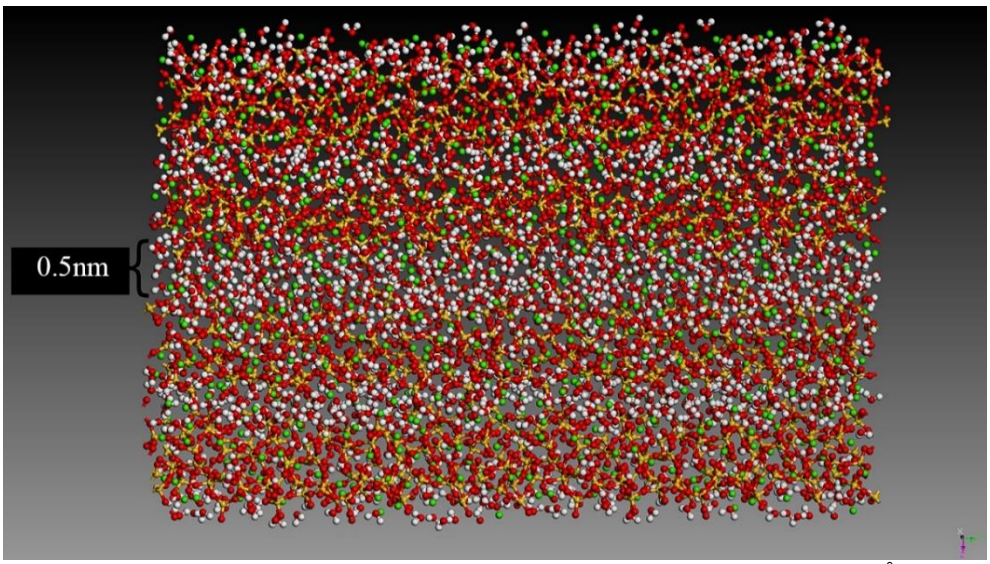

Figure 2: Structure of CSH layers with a 0.5 nm cavity between two layers Tobermorite 14Å (red: oxygen, yellow: silicon, white: hydrogen, green: calcium)

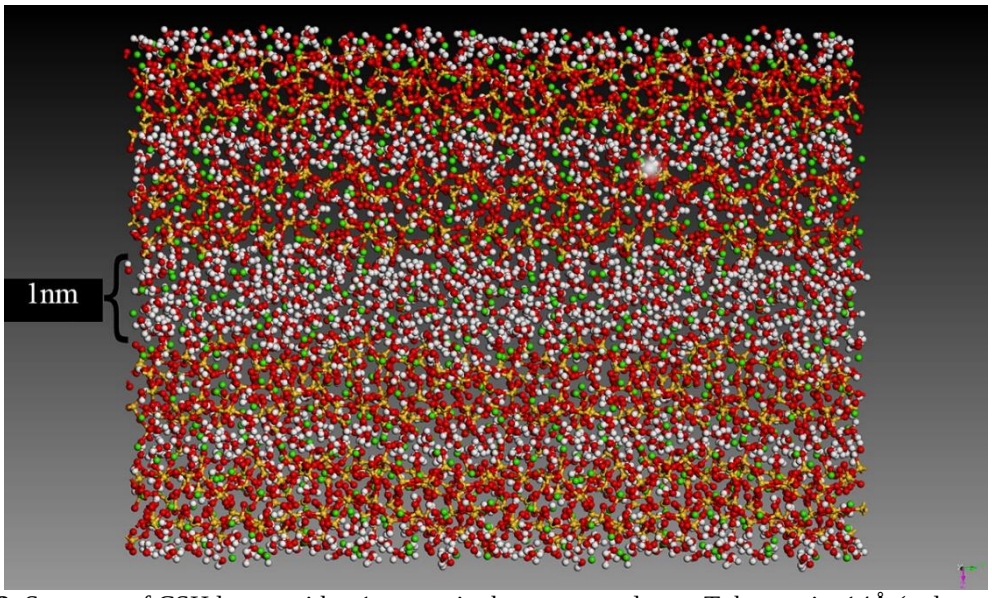

Figure 3: Structure of CSH layers with a 1 nm cavity between two layers Tobermorite 14Å (red: oxygen, yellow: silicon, white: hydrogen, green: calcium)

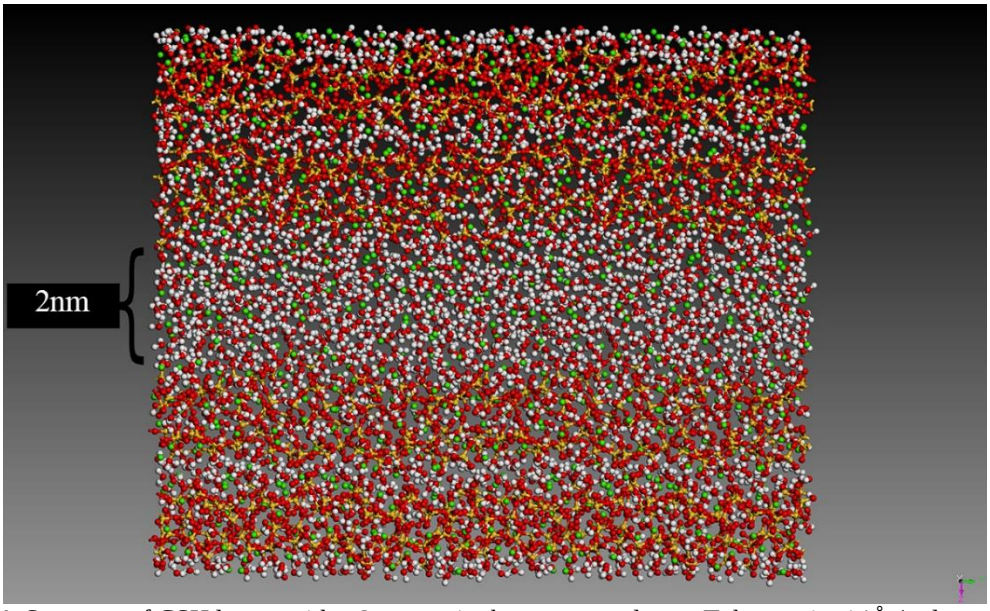

Figure 4: Structure of CSH layers with a 2 nm cavity between two layers Tobermorite 14Å (red: oxygen, yellow: silicon, white: hydrogen, green: calcium)

3 RESULTS AND DISCUSSION

The elastic modulus of the three models prepared in accordance with the Section 2 is obtained. The results of the elastic modulus are shown in Table 3.

Table 3: Elastic modulus of models.

Model	0.5 nm cavity	1 nm cavity	2 nm cavity
Elastic modulus (GPa)	48.23	44.47	30.55

As the dimensions of the cavity increase, the amount of water absorbed in the cavity increases and this leads to a decrease in the elastic modulus of CSH. Water occupies space, and this occupation of space leads to the distances of the chains from each other. This distance of the chains reduces the bond strength between the chains and the calciums that are associated with them, and this leads to weaker bonds as well as a reduction in the elastic modulus. On the other hand, the presence of water leads to the formation of new hydrogen bonds. Due to the fact that hydrogen bonds are weaker bonds than ionic bonds, these bonds weaken the bond between atoms. In the dry state, the bond between the calcium atom and the silicate chain is an ionic bond, while in the presence of water, the hydrogen bond is mediated by the presence of water between the two chains, which weakens the bonds. As the number of water molecules increases, more intermediate bonds are formed between the water molecules and as a result more hydrogen bonds are formed, which leads to a decrease in the elastic modulus.

4 CONCLUSION

In this study, the modeling of interlayer cavities and the effect of these cavities on the elastic modulus of CSH were investigated. For this purpose, in this study, the molecular dynamics method was used. The results showed that increasing the size of the cavities reduces the amount of elastic modulus. Due to the greater water uptake in larger cavities, this was explained by the increase in hydrogen bonds and the decrease in the strength of chemical bonds in CSH.

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