A molecular dynamics and microporomechanics study on the mechanical properties of major constituents of hydrated cement[1]

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Abstract:

This paper presents a framework for using Molecular Dynamics (MD) simulations for estimating the mechanical properties of major constituents of hydrated cement: Calcium-Silicate-Hydrate(C-S-H) and Calcium Hydroxide (CH). Microporomechanics technique is used to calculate properties of two types of C-S-H concentrations, namely, low density (LD) and high density (HD) C-S-H gels. From the analysis, we found that the Young's modulus of C-S-H structurally related jennite and tobermorite 14 Å are 66.9GPa and 43GPa, respectively. Calculated poroelastic properties of LD and HD C-S-H are 30.8GPa and 41GPa.

Key words: mechanical properties, molecular dynamics, microporomechanics, C-S-H, hydrated cement

1. Introduction

Cement is one of the most widely used materials on earth. The US annual consumption of cement is estimated to be about 2.35 billion tons per year [1-2]. Since cement is usually produced at high temperatures, its production emits high carbon dioxide (CO_2). Cement production accounts for an estimated 5 to 10 percent of the world's CO_2 emissions and is one of the primary greenhouse contributors to global warming [1-2]. In the past, researchers believed that the durability and strength of concrete were due to the binding properties of cement. However, researchers at Massachusetts Institute of Technology reported that the strength and durability of concrete are due to the structure of the cement nanoparticles [1-2]. This discovery can lead to major reductions in carbone dioxide emissions during manufacturing process. If engineers can reduce total CO_2 emission by 10 percent, that would accomplish one-fifth of the Koyoto Protocol's goal of 5.2 percent reduction of CO_2 emission. Therefore it is important to take the research one step further into the understanding of the relationship between cement properties and its nanostructure, in hope to eventually lead to new designs for environmentally friendly cement materials.

When Portland cement is dispersed in water, different hydration products are formed. Calcium silicate hydrate (C-S-H) comprises 50-60 percent of the volume of solids in completely hydrated cement paste. Crystal structures of C-S-H are closely related to mineral crystals of tobermorite 14 Å and jennite. Calcium hydroxide (CH) crystal (also called portlandite) comprises 20-25 percent of the volume of solids in the hydrated paste. Other components of hydrated cement paste include calcium sulfoaluminate, unhydrated clinker grains and voids [3].

The dimension of the typical hydration products of cement is roughly between 1 to 100 nm, which meets one of the requirements of the definition of nanotechnology proposed by Ratner [4-5]. Therefore, it is quite rational to use nanomechanics to study the mechanical behavior of such material. In this paper we first employ the molecular dynamics method to estimate the mechanical properties of major constituents of hydrated cement.

In this paper the nano-mechanical properties of cement hydrates are calculated using the molecular dynamics technique. Then the micro-mechanical properties of low density (LD) and high density (HD) C-S-H gels are estimated using the microporomechanics techniques. This paper and the authors' related works [6-8] are intended to set a framework for understanding the relationship between the chemical composition, microstructure morphology and mechanical properties of concrete constituents (e.g, unhydrated cement, hydrated cement, sand and gravel).

2. Nanostructure of hydrated cement

Among the major constituents of hydrated cement paste, C-S-H is no doubt the most important and complicated constituent. The revealing of C-S-H and cement gel structure began with the milestone work conducted by Powers, et al. [9-11], when they proposed a colloidal and gel-like C-S-H model as shown in [9]. According to Powers et al. [9-11], the cement gel contains colloidal C-S-H and noncollodial calcium hydroxide (CH). The gel particles were once regarded as spheres, but were later determined to be platy, or ribbonlike, fibers. The porosity in the Powers gel model was estimated to be around 28%. Recently Jennings [12-14] published a series of papers on a widely accepted C-S-H colloidal model that is shown in Figure 1. In this model, two types of C-S-H are considered: Low Density (LD) and High Density (HD) cement gels which have 37% and 24% gel porosity, respectively. Both LD and HD C-S-H are formed by the basic building block 'Globules' which has the dimension of 5.6nm and an 18% nanoporosity filled with structural water. Gel porosities of C-S-H and nanoporosity of globules are intrinsic properties of concrete, which means they remain the same in any type of C-S-H. Moreover Jennings found that, the volumetric proportion of LD C-S-H and HD C-S-H changes from one cement paste to another, depending on the water-cement ratio. In the development of the microstructure of cement, HD C-S-H is usually formed around residual cement clinkers; while CH is generally formed in between LD C-S-H and adjacent to macropores [15].

Exact morphology of C-S-H was, first, proposed by Taylor [16-17]. Taylor's model, called the T/J model, claimed that C-S-H had a disordered layer structure where most of the layers were composed of structurally imperfect jennite and the rest were formed from structurally related tobermorite. Another model was studied by Richardson and Groves [18-19] and called T/CH model. The T/CH model treated C-S-H as a tobermorite-'solid solution' calcium hydroxide which involves a tobermorite-like structure interstratified with layers of calcium hydroxide [20]. Since Richardson and Groves' model is a constitutional model in nature, we adopted Taylor's T/J C-S-H gel structure model in our simulation. The exact nanostructure of the C-S-H disordered layer structure has not yet been decrypted, while structure-related crystals tobermorite 14Å and jennite are recently given by Bonaccorsi, et al. [21-22]. Manzano, et al. [23] simulated the mechanical properties of crystalline C-S-H gel compounds with the lattice dynamics method. The Young's moduli they calculated were 91 GPa for tobermorite 14 Å and 66 GPa for jennite.

It is relatively difficult to perform direct mechanical testing to measure the properties of the solid C-S-H and only limited work is reported in the literature. Ulm, et al. [15, 24] used the nanoindentation technique and micorporomechanics theories to calculate the solid phase elastic modulus indirectly.

In this paper, the molecular dynamics approach using commercially available Materials Studio software [25] is used to obtain properties of jennite and tobermorite 14 Å. The crystal structure of 14 Å tobermorite is obtained from the latest finding by Bonaccorsi, et al. [21]. Tobermorite 14 Å has the chemical formula $Ca_5Si_6O_{16}(OH)_{2.7}H_2O$. The most distinguished characteristic of tobermorite 14 Å is that it has a typical layer structure as shown in Fig. 2. Water molecule is trapped between calcium polyhedra layers. The crystalline structure is formed by a central sheet with CaO_2 stoichiometry, connected on both sides to silicate chains with a periodicity of three tetrahedra (dreierketten, or wollastonite-like chains). It is expected to have anisotropic material properties from MD computation due to the platy nature of the crystal structure as shown in Fig. 2. The crystal structure of jennite [2] (Fig. 3.) is built up by three modules: ribbons of edge-sharing calcium octahedra, silicate chains of wollastonite-type, and additional calcium octahetra.

Calcium Hydroxide (CH, also called portlandite), which constitutes 20-25% of the volume of solids in the cement paste, usually forms large crystals with hexagonal-prism morphology (Fig. 4). CH usually forms much larger crystals than C-S-H particles with a hexagonal-prism or platy shape. The crystalline structure of Calcium Hydroxide is shown in Fig. 4.

3. Methods and results

3.1 Molecular dynamics simulation of C-S-H solid and CH

We used the molecular dynamics simulation to obtain the mechanical properties of solid C-S-H, and CH. Molecular dynamics is one of the modeling schemes of molecular mechanics which directly calculate the potential energy by solving for the classic Newton's equation of motion:

$$-\frac{dE}{dR} = m\frac{d^2R}{dt^2} \tag{1}$$

where E is the potential energy, R represents the position of the nuclei, m is mass and t is time. The solution of Newton's equation in MD needs an empirical fit to the potential energy surface, which is often called a forcefield [25]. After the dynamics simulation has been performed, we analyzed the resulting deformed molecular structure to determine its elastic constants. The elastic constants of the final atomic configuration were computed using the static approach suggested by Theodorou and Suter [26]. The elastic constants in this approach are defined as:

$$C_{lmnk} = \left.\frac{\partial \sigma_{lm}}{\partial \varepsilon_{nk}}\right|_{T,\varepsilon_{nk}} = \left.\frac{1}{V_o}\frac{\partial^2 A}{\partial \varepsilon_{lm}\partial \varepsilon_{nk}}\right|_{T,\varepsilon_{lm},\varepsilon_{nk}} \tag{2}$$

where C is stiffness constant, σ represents the stress component, ε is the strain component, A denotes the Helmholtz free energy, and V_o is the volume of the simulation cell in the undeformed configuration. We calculated the corresponding isotropic polycrystalline elastic moduli based on the corresponding single-crystal elastic constants by the Oigt-Reuss-Hill (VRH) approximation [27-28]. More details on MD and mechanical properties calculation can be found in [6]. Molecular mechanics simulation conditions and basic input information regarding the structures are shown in Tables 1 and 2, respectively. The MD simulation results for tobermorite

14 Å, jennite and CH, are given in Tables 3-5. The Young's moduli of tobermorite 14 Å, jennite and CH calculated by MD are 43GPa, 66.9 GPa and 51.5GPa; while the values given in the current literature are: 91GPa, 66GPa and 42.3GPa. Compared to the values existing in the literature, MD yields fair results for jennite and CH. However, there exists a large difference for tobermorite 14 Å.

3.2. Micropormechanics effective properties calculation of LD and HD C-S-H

C-S-H gel is a porous material with 37% (LD) and 24% (HD) porosity. Microporomechanics is a very useful tool to study the mechanics and physics of multiphase porous materials [27]. According to [4], the poroelastic properties of LD and HD C-S-H can be derived by:

$$K = G_s \frac{4\left(1-\phi_0\right)}{3\phi_0 + 4(G_s / K_s)} \tag{3}$$

$$G = G_s \frac{\left(1-\phi_0\right)(8G_s + 9K_s)}{6\phi_0(2G_s + K_s) + 8G_s + 9K_s} \tag{4}$$

where *K* and *G* are effective bulk and shear moduli, G_s and K_s represent shear and bulk modulus of the solids, and ϕ_0 is porosity.

Based on Taylor’s T/J C-S-H model, the majority of C-S-H solids are jennite type. Therefore, we used mechanical properties of jennite obtained from MD simulations to represent the solid properties needed in equations (3)-(4) to compute the effective properties *K* and *G* of LD and HD C-S-H. The results are shown in Table 4. LD and HD C-S-H moduli are calculated as 30.8 GPa and 41GPa. From the computed properties of two types of C-S-H shown in Table 4, it is observed that there is a relatively large difference between our obtained values and the ones obtained using the lattice dynamics[23]. More investigation is needed to explain this difference.

4. Discussions and conclusions

We attempted to use molecular dynamics method to compute the mechanical properties of major constituents of hydrated cement. The computed mechanical properties for CH and jennite are comparable to those reported in the literature. This gives us some confidence in using MD as a tool for simulation of cement-based materials at nano scale. However, there still exist some uncertain areas. For example, the simulated results are dependent on the specific forcefield and the simulation supercell size. A general rule has not been developed regarding their selection. These are important issues that need to be addressed in the future in order for the MD to be a reliable tool. Another important issue is that, in order to have an accurate result, we need to know the real amorphous structure of C-S-H. This structure, at the moment, is not yet fully understood.

Results of micropormechanics and MD simulations of solid C-S-H, can be used to compute the effective properties of two types of C-S-H,.The accuracy of the final results depends on the quality of values of solid C-S-H.

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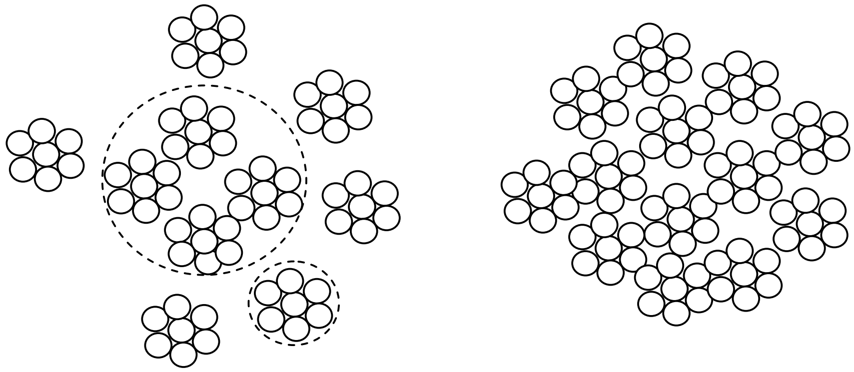

(a) (b)

Fig. 1. Two Types of C-S-H (a) LD (b) HD

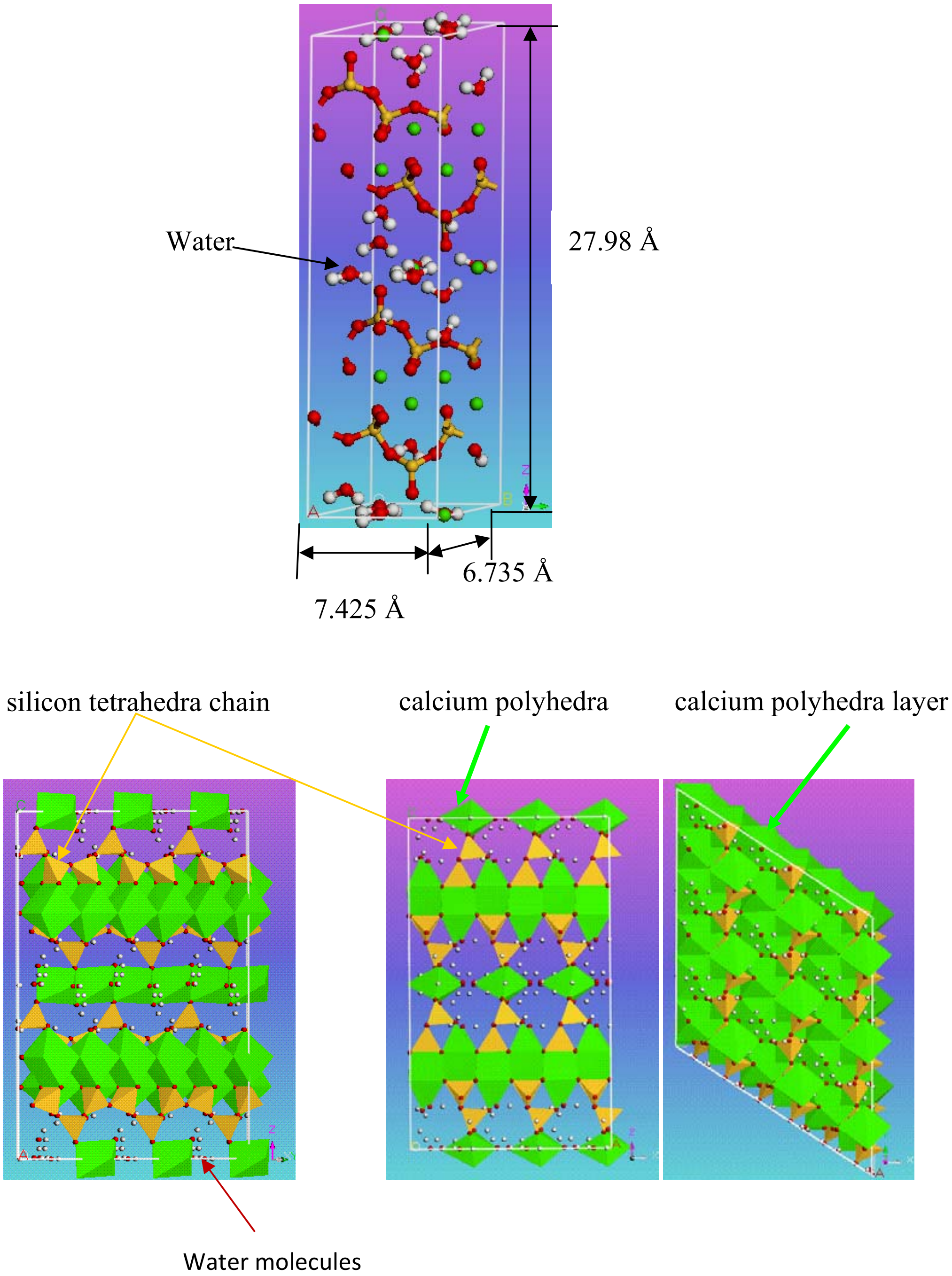


Fig. 2. Unit Cell of Crystal 14 Å tobermorite (a) Perspective (b) Different Views of a Supercell Structure of 14 Å Tobermorite

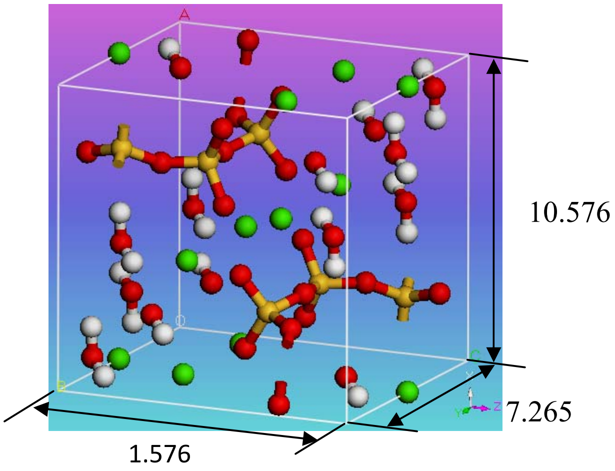


Fig. 3. Unit Cell of Crystal Jennite Perspective View (Å)

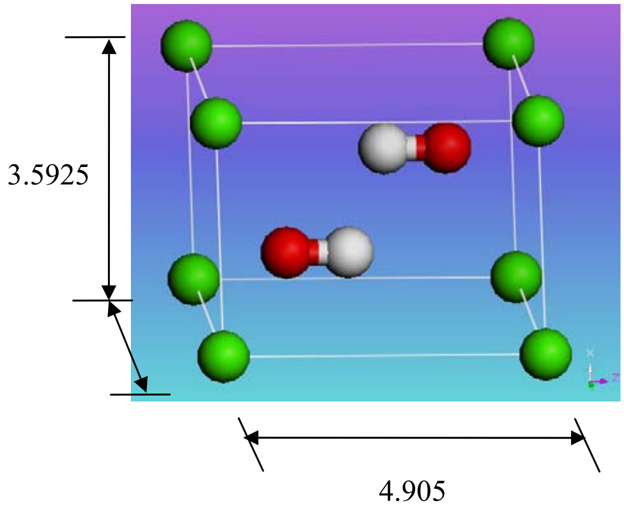


Fig. 4. Unit Cell of Crystal Calcium Hydroxide (Å)

Table 1. Molecular Mechanics Simulation Conditions

Name of Condition	Conditions Used in This Study		
	Tobermorite 14 Å	Jennite	CH
Cell Size (Å)	6.735×7.425×27.987	10.576×7.265×10.931	3.5925×3.5925×4.905
No. of Atoms	124	69	5
Molecular Tools	Discover or Forcite	Discover or Forcite	Discover or Forcite
Force Fields	Compass, Universal	Compass	Compass
MD Ensemble	NPT	NPT	NPT
Temperature (^{0}C)	25	25	25
Temperature Control (GPa)	Andersen or Nose	Andersen or Nose	Andersen or Nose
Pressure	0.001	0.001	0.001
Pressure Control	Parrinello or Berendsen	Parrinello or Berendsen	Parrinello or Berendsen
Time Step (fs)	1	1	1
Dynamics Time (ps)	100~400	100~400	100~400

fs: femto sec. ps: pico sec.

NPT: N-constant number of particles in the simulation system P: constant pressure T: constant temperature

Table 2. Cell Parameters of Crystal Tobermorite 14 Å, Jennite and CH

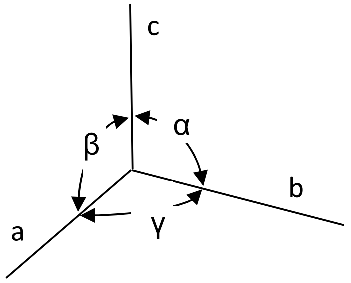
Crystal System	tobermorite	Jennite	CH
Lattice type	Monoclinic	Triclinic	Trigonal
a [Å]	6.735	10.576	3.5925
b [Å]	7.425	7.265	3.5925
c [Å]	27.987	10.931	4.90
$\alpha[^o]$	90	101.30	90
$\beta[^o]$	90	96.98	90
$\gamma[^o]$	123.25	109.65	120
Notation			

Table3. Molecular Simulation Results of Tobermorite 14 Å

Supercell Properties	1a×1b×1c*		2a×2b×2c		Literature Values[21]
MD Tools & Forcefields	F-U	D-C	F-U	D-C	
E(GPa)	42.94	**43.01**	-	51.4	91
ν	0.29	**0.343**	-	0.328	0.17
K(GPa)	33.4	**45.68**	-	49.79	46.0
G(GPa)	16.7	**16.01**	-	19.35	39

* a, b, and c are dimensions of the unit cell of the crystal structure.

F: Forcite, U: Universal, C: COMPASS

Table4. Molecular Simulation Results of Jennite

Supercell Properties	1a×1b×1c		2a×2b×2c		Literature Values[23]
MD Tools & Forcefields	F-C	D-C	F-C	D-C	
E	44.1	82.2	66.9	-	66
ν	0.28	0.33	0.34	-	0.24
κ	33.3	78.4	69	-	43
G	17.2	31.0	25	-	26

Table 5. Molecular Simulation Results of CH

Supercell Properties	1a×1b×1c		2a×2b×2c		3a×3b×3c		Literature Values[31]
MD Tools & Forcefields	D-C	F-C	D-C	F-C	D-C	F-C	
E(GPa)	152	**51.5**	195.	74.5	22.4	65.2	42.3
ν	0.16	**0.31**	0.31	0.28	0.45	0.3	0.324
K(GPa)	180.5	**44.6**	174.6	56.9	77.3	55.5	40
G(GPa)	109.3	**19.7**	74.3	29.1	7.7	25	16

Table 6. Computation of LD and HD Mechanical Properties

C-S-H	**Porosity** ϕ_0	**K_s**	**G_s**	**E**	**E_{ref}**	**ν**	**$ν_{ref}$**
LD	37%	25	69	**30.8**	21.7[30] 23.4[32]	0.29	0.24[30]
HD	24%	25	69	**41**	29.4[30] 31.4[32]	0.3	0.24[30]