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COMPUTATIONAL MODELING OF MULTI-SCALE MATERIAL FEATURES IN CEMENT PASTE – AN OVERVIEW

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Abstract. *Computational modeling of complex, heterogeneous, multi-scale features of cement paste requires starting from their fundamental building blocks that includes material chemistry, microstructural morphology. This would enable capturing scale relevant features that influence the properties and behavior of materials through associated computational, material and mechanistic models. Such modeling starting from nanoscale material features through material chemistry modeling via molecular dynamics (MD); modeling of complete three-dimensional virtual microstructure including the evolution of microstructure due to hydration of cementitious materials are briefly highlighted. Material chemistry modeling discussions from our recent work on nanoscale shear deformation to obtain the stress-strain behavior solely based on the material chemistry structure of hydrated cementitious material constituent CSH Jennite is summarized. Micro-scale modeling involving finite element based repeated volume element (RVE) modeling applied to the virtual three-dimensional complex microstructures at different degrees of hydration of the cement paste is also summarized. Complete details are presented in our other current and future publications in the literature. Multi-scale modeling that links across various length scales and material features in complex heterogeneous material systems provides an effective way of coupling material science and engineering features for their better understanding and tailored material design. These approaches present a new future direction for integrated material science and engineering of materials and structures.*

1 INTRODUCTION

Cementitious materials, an excellent example of highly complex, heterogeneous material systems, are cement-based systems that include cement paste, mortar, and concrete; though commonly used are one of the most complex in terms of material morphology and structure than most materials, for example, crystalline metals. Processes and features occurring at nanometer sized morphological structures affect the performance, deformation/failure behavior at larger, engineering length scales. In addition, cementitious materials undergo chemical and morphological changes gaining strength during the transient hydration process. Hydration in cement is a very complex process creating complex microstructures and the associated molecular structures that vary with hydration. Multi-scale modeling of such material systems requires starting from fundamental building blocks for the analysis and understanding at each of the disparate length scales capturing the scale relevant features through associated computational models. In conjunction, techniques to correlate and transcend across the morphological features at each of the length scales, and associated computational coupling techniques across the multiple scales are required. In this paper, recent work from our research group on the nano to continuum level modeling of cementitious materials is highlighted.

This paper discussions are with an emphasis on the computational modeling at different length scales building the foundations of our research work consisting of,

- Molecular Dynamics (MD) modeling for the nano scale features of the cementitious material chemistry.
- Micro-mechanics modeling employing the cement microstructure morphology that takes into account the variations in the morphological features.

Brief discussions of our on-going work on the scale relevant modeling of the multi-scale heterogeneous cementitious materials are presented in this paper to provide a forum for technical interactions and collaborations on the current state of the art, technology and research coupling material science and engineering.

2 NANOSCALE MATERIAL CHEMISTRY LEVEL MODELING

Portland cement in the powder form consists of four different major constituents: Tri-Calcium silicate (C_3S), Di-Calcium silicate (C_2S), Tri-Calcium aluminate (C_3A), and Tetra calcium aluminoferrite (C_4AF) [1]. Hydration of cement is the chemical reaction between cement compounds and water, which cause hardening of cement forming the heterogeneous composite material. The most important hydrated cement product is Calcium Silicate Hydrate (CSH). Due to the complexity of CSH, molecular structure of CSH has not been fully resolved yet. Other naturally occurring minerals Jennite [2] and Tobermorite14 [3] molecular structures are the closest representation of CSH crystal that are accepted in the field. In these chemical formula representations, the notation common in the cementitious material community is followed: C refers to CaO; S refers to SiO_2, A refers to Al_2O_3, F refers to Fe_2O_3, and H refers to H_2O.

MD is employed in modeling materials science and biomolecules to study and investigate structure and behavior of the interacting atoms of any molecular system. The methodology is based on transient dynamics analysis of atoms represented by system of particles based on classical Newtonian mechanics. The transient dynamic atomistic configurations under varying thermodynamic state conditions is coupled with statistical mechanics to obtain the predicted, thermo-physical properties as well as molecular level behavior of material systems based on their atomistic positions and velocities.

The total potential energy for the material system varies for different molecular types based on associated molecular parameters and atoms. The potential energy of the CSH Jennite molecular structure in our research is determined using a COMPASS force field in the present work. The functional form of the COMPASS (condensed-phase optimized molecular potentials for atomistic simulation studies) contains three major terms, which are bond terms, non-bond terms, and cross terms [4]. Bond terms include bond stretch, angle bending, angle rotation, and out of plane angle terms, associated with molecular, material chemistry level configuration of hydrated cement paste CSH Jennite structure.

3 MICRO SCALE MODELING

The advent of scalable computing capabilities makes it possible to model large molecular and representative volume element (RVE) based material systems. Individual elastic properties and density for clinkers, unhydrated and hydrated products are usually and can be further estimated through molecular dynamics simulations. These properties could then be utilized in the microscopic level RVE simulations. The representative volume element (RVE) is defined as the smallest volume of material that captures the global characteristics of the material. Random results for overall properties of the material will be obtained if the tested volumes are smaller than this statistically representative sub-domain of the microscopic geometry. Such a volume must be sufficiently large to allow a meaningful sampling of the micro-scale stress and strain fields as well as sufficiently small for the influence of macroscopic gradients to be negligible, and for an analysis of these micro fields to be possible.

CEMHYD3D Ver. 3, developed by NIST (National Institute of Standards and Technology, USA), was used to simulate the hydration process and formation of the digitally generated virtual microstructure for a typical Type-I general purpose cement [5]. CEMHYD3D allows creation of a starting three-dimensional microstructure based on a measured geometrical particle size distribution (PSD), volume fractions and surface area fractions of the constituent phases for the cement powder, extracted from 2D composite SEM (scanning electron microscope) images of cement at various degrees of hydration and modeling the hydration kinetics [5].

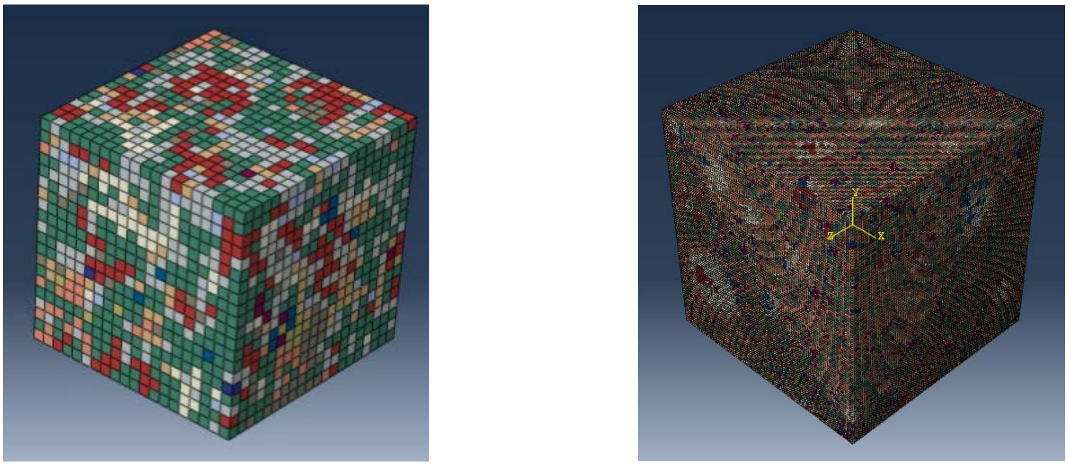

Figure 1: 100x100x100 micron finite element model (left) and hydrated cement microstructure (right) [7].

The three-dimensional virtual microstructure is modeled as a micro-scale representative volume element (RVE) in a finite element analysis code to generate cubes of several microns in dimension and subjected to various prescribed deformation modes to obtain the effective elastic tensor of the material. The micro-structure voxel information generated by CEMHYD3D is imported into the general purpose ABAQUS® finite element code using an in-house developed Matlab® code and meshed using continuum hexahedral (C3D8) elements to generate RVE domains of various dimensions (Fig. 1). Microstructure analysis based on cement RVE considered both periodic boundary condition (PBC) and kinematic boundary conditions (KBC). RVE calculated elastic properties such as moduli are compared with the values obtained for this complex material microstructure configuration via asymptotic expansion homogenization (AEH), originally developed for woven fabric composites [6]. Complete details are available in reference [7].

4 RESULTS AND DISCUSSIONS

Brief discussions of key results from shear deformation and failure of nanoscale CSH Jennite are presented next. Complete details are available in reference [8].

4.1 Nanoscale shear deformation of CSH Jennite

The molecular/chemistry level structure of CSH Jennite is defined by a triclinic unit cell of dimensions a=10.6 Å, b=7.3 Å, c=10.9 Å, and angles α=101.3°, β=97.0°, γ=109.7°. In Figure 2 a crystal of CSH Jennite, consisting of 64 unit cells in a 4x4x4 arrangement, is illustrated. The molecular structure of jennite is layered, formed by sheets of calcium oxide connected to short silica chains, three silica monomers long, that are not connected to each other. The calcium oxide sheets are linked to each other by additional calcium octahedral sites. The layers containing the calcium octahedral sites connecting the calcium oxide sheets also contain most of the free water molecules in the structure.

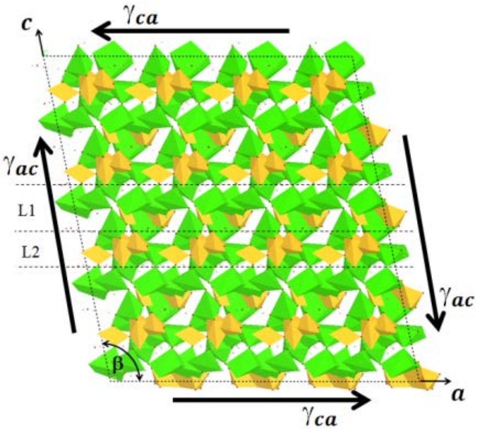

Figure 2: Molecular structure of nanoscale CSH Jennite viewed across the (ac) crystallographic plane. Arrows indicate the direction of the shear stress simulated [8].

As a load-bearing system, nanoscale CSH Jennite can be considered as a structure in which interconnected layers of calcium oxide are responsible for the structural integrity of the system. The short silica chains distributed on calcium oxide layers can be considered to act as nanoscale reinforcements. These short silica chains are not bonded to each other but only to the calcium oxide layers; hence they cannot be considered as the load-bearing skeleton of the structure. Based on the structural characteristics of nanoscale CSH Jennite illustrated above, results from mechanical behavior of the material under shear deformation and the changes produced by the deformation applied on the calcium oxide layers are briefly illustrated. Complete details of MD modeling methodology and shear deformation of nanoscale CSH Jennite are available in reference [8].

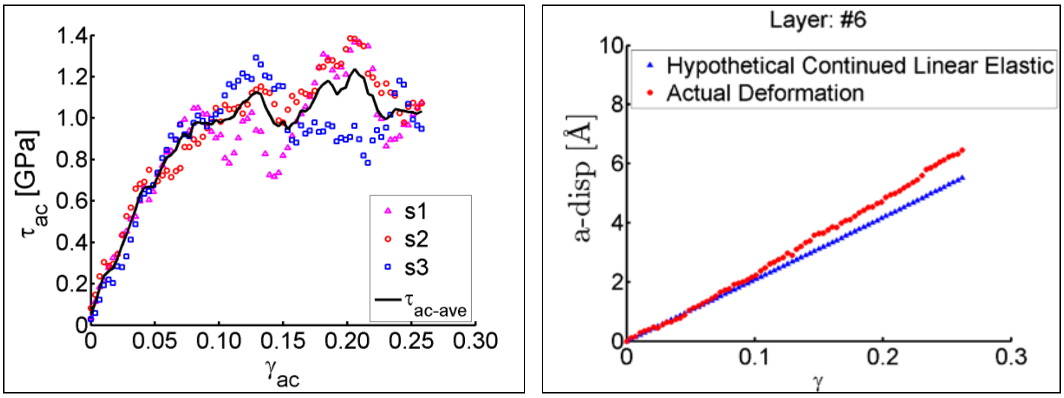

Figure 3: Shear stress-strain behavior of nanoscale CSH Jennite from MD (left); center of mass displacement (continued linear elastic vs. actual) [ ].

Figure 3 presents the shear stress-shear strain behavior obtained from shear deformation of nanoscale CSH Jennite built upon 64 unit cells. MD computational analysis experiments were repeated using three different initial configurations of the material chemistry structure and show a good, repeatability of the linear and non-linear transition. The shear deformation is characterized by a linear region followed by a non-linear transition at a strain of about 0.08. Shear modulus obtained from the chemistry level modeling is 11.2±0.7 GPa. Layered structure of the predominant calcium oxide in the molecular structure indicates that shear deformation is primarily due to sliding of calcium oxide layers. The computed displacement after the onset of non-linear region is larger than the displacement with a continued elastic deformation. This is further indicated by a change in slope of the computed displacement curve as seen in Figure 3 (right). This correlates well with the transition from linear to non-linear behavior of the stress-strain plot shown in Figure 3 (left). Complete discussions are presented in reference [8].

4.2 Microstructural orthotropic elastic matric predictive modeling of cement paste

RVE analysis of cement microstructure involved six axial and 6 shear deformation cases resulting in the orthotropic elastic matrix. The corresponding effective engineering constants of the bulk properties are obtained. Table 1 presents the effective properties obtained from elastic tensors based on kinematic boundary conditions (KBC), periodic boundary conditions (PBC) applied to 3D cement virtual microstructure, as well as the results from asymptotic expansion homogenization (AEH). CSH gel formation in the cementitious materials increasingly support the mechanical stresses in the microstructure as the hydration proceeds, and is noted in the corresponding increase in the elastic modulus (E) and shear modulus (G) values. Also, due to the increase in CSH gel volume fraction and reduction in other unhydrated component fractions, microstructure also tends to become nearly isotropic with higher degree of hydration. The difference between the PBC and KBC conditions is found to be smaller (< 4%). Elastic modulus and shear modulus values obtained from AEH estimates are slightly higher than the KBC and PBC estimates. Complete details are presented in reference [7].

5 CONCLUDING REMARKS

Complex heterogeneous material systems with material features ranging from nano to macro scales require multi-scale modeling analysis for their understanding at each of the disparate length scales capturing the scale relevant features through associated computational models. Such computational models for complex heterogeneous material systems should not only be limited to homogenized engineering scales, but also need to include and emulate the effects of the morphological variations and material chemistry changes that impact the material properties and behavior at engineering length scale as discussed for cementitious materials.

Method	Domain Size (microns)	DOH	G (GPa)	E (GPa)
KBC	100x100x100	0.8	9.08	24.20
		0.3	5.71	16.39
PBC	100x100x100	0.8	9.35	24.69
		0.3	6.39	17.65
AEH	100x100x100	0.8	9.15	24.05
		0.3	5.88	15.79

Table 1: Mechanical properties of cement paste from microstructure RVE analysis.

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