



Nano-scale investigation of elastic properties of hydrated cement paste constituents using molecular dynamics simulations



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ABSTRACT

Hydrated cement paste (HCP), which is present in various cement-based materials, includes a number of constituents with distinct nano-structures. To understand the elastic properties of the HCP at the nano-scale, a comprehensive set of crystalline structures that represent the main HCP constituents is developed for Molecular Dynamics (MD) simulations. The accuracy of estimated values is verified by comparing them with the results from experimental tests and other atomistic simulation methods. The outcome of MD simulations is extended to predict the elastic properties of the C–S–H gel by rescaling the values calculated for the individual crystalline structures. To take into account the contribution of porosity, a detailed microporomechanics study is conducted on low- and high-density phases of C–S–H. The obtained results indicate that MD simulations are capable of capturing the elastic properties of the C–S–H gel. This is further verified by comparing the rescaled values with the predictions from nanoindentation tests.

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1. Introduction

Cement-based materials, such as mortar and concrete, are widely used in the construction of civil infrastructure components. This is mainly due to the availability of raw materials, fire resistance, and cost advantages. There are, however, certain concerns regarding the strength and durability of cement-based materials during their service life. To address this issue, several research efforts have been made to understand the main properties of cementitious materials. These efforts include both experimental and numerical studies, most of which have been carried out at the macro-scale to improve the serviceability and performance of concrete structures (e.g., [9,13,59,66]). Despite the wealth of knowledge currently available, there is still a gap in the literature concerning the main properties of the hydrated cement paste (HCP) as the most important component of cement-based materials. Considering the fact that hydrated cement binds the aggregates together and directly contributes to the structural characteristics of concrete as a composite material, an in-depth study of the HCP phases in smaller scales (i.e., micro- and nano-scale) provides invaluable information about the key mechanical properties of concrete and identifies appropriate methods to improve them.

The HCP is formed as a rigid phase following the chemical reactions between the Portland cement and water. This phase is found to be a highly complex composite made of several crystals, each of which contributes to the mechanical strength and performance of concrete. The cement paste hydration products can be categorized into four major groups: (i) calcium silicate hydrates (C–S–H), (ii) calcium hydroxide (portlandite), (iii) calcium aluminate monosulphate hydrates (AFm), and (iv) calcium aluminate trisulphate hydrates (Aft). The C–S–H constitutes 50–60% of the total volume of the solid HCP. This percentage changes to 20–25% for the portlandite and 15–20% for the AFm and Aft combined. Among the hydration products, the C–S–H has an amorphous nanostructure, which is difficult to be characterized. There are, however, few crystals that can mimic the structure of the C–S–H. Tobermorite 9, 11, and 14 Å as well as jennite are the crystals frequently used in the literature to investigate the structural and mechanical properties of the C–S–H. On the other hand, ettringite and monosulphoaluminate have been identified as the most common phases of the Aft and AFm structures, respectively.

Among various crystalline structures proposed for the HCP, the elastic properties of portlandite have been determined using experimental studies, including Brillouin spectroscopy [26], tests of compacted powder samples of portlandite with different porosities [4,70], and compression tests [36]. Based on the available experimental results, Monteiro and Chang [43] calculated the elastic properties of portlandite from the mathematical morphol-

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ogy of concrete while Laugesen [33] provided another set of calculations using the density functional theory (DFT). Speziale et al. [60] estimated the elastic properties of natural calcium hydroxide, including all the adiabatic elastic constants and acoustic velocities, using the Brillouin spectroscopy in the ambient conditions. A similar effort was made by Speziale et al. [61] to determine the single-crystal elastic constants of natural ettringite. It was concluded that ettringite is approximately 30% less stiff than portlandite. Nanoindentation experiments have also been used to directly find the Young's modulus and Poisson's ratio of the C–S–H gel. The conducted experiments, which cover a range of water-to-cement (w/c) ratios, include Hughes and Trtik [27], Constantinides and Ulm [12], Zhu et al. [74], and Vandamme et al. [67]. In a more recent study, Oh et al. [47] employed high-pressure synchrotron X-ray diffraction (XRD) tests to determine the bulk modulus of the crystalline structure of tobermorite 14 Å. It should be noted that except the listed studies, no experimental results are available in the literature regarding the elastic properties of the tobermorite family, jennite, and other hydrated phases.

To quantify the mechanical properties of the HCP at the micro- and nano-scale, various atomistic simulation methods have been employed. Manzano et al. [37,38] used Molecular Mechanics (MM) simulations to derive the elastic properties of various HCP phases considering the composition of their crystals. Pellenq et al. [50] examined a number of atomistic simulation methods to improve the mechanical properties of cementitious materials with a special focus on C–S–H. Shahsavari et al. [58] presented first-principle calculations to estimate the elastic constants of the tobermorite family and jennite based on the interlayer interactions. Zaoui [73] investigated the structural properties of tobermorite 11 Å by MM simulations under a pressure ranging from 0 to 30 GPa. To check the transferability of the potentials employed, the DFT calculations were provided for the fixed pressure of 15 GPa. More recently, Dharmawardhana et al. [16] evaluated the electronic structure and interatomic bonding of the four major C–S–H components (i.e., tobermorite 9, 11, 14 Å, and jennite) following the *ab initio* methods and discussed the role of interatomic bonding in the mechanical properties of the C–S–H crystals. A review of studies conducted on the HCP at the nano-scale indicates that while MM and *ab initio* methods have been frequently utilized for atomistic simulations, there is no comprehensive study on the elastic properties of the HCP constituents using Molecular Dynamics (MD) simulations.

The MD method is known as one of the most powerful atomistic simulation methods, through which the equilibrium thermodynamic properties of a system are calculated by tracking the atoms that exist in the system during a certain period of time. This method has been used to characterize the mechanical properties of a wide range of materials, including natural materials (e.g. wood cell wall layers, native metals, and clays), biological materials (e.g. proteins and DNA), composite materials, polymeric materials, and ceramics. Han and Elliott [20], Wen et al. [69], Deng et al. [14], Le et al. [34], Anoukou et al. [5], Chen et al. [10], and Lee et al. [35] are examples of the most recent studies that have efficiently utilized the MD method. In this paper, a detailed study is presented on how the capabilities of the MD simulations can be used to determine the elastic properties of the main constituents of HCP. This study examines a complete range of crystalline structures, including portlandite, tobermorite 9, 11, 14 Å, jennite, ettringite, kuzelite, and hydrogarnet. To evaluate the precision of simulations, the MD results are compared with an extensive set of experimental and simulation data published in the literature for each of the HCP phases. While this study captures the elastic properties of all the C–S–H components at the nano-scale, a major difference is observed between the values obtained for the individual C–S–H components compared to the ones suggested for the whole C–S–

H gel. This difference can be understood by considering the intrinsic nano-porosity present in the C–S–H gel. Hence, a separate microporomechanical study is performed to relate the corresponding elastic properties. This is achieved by utilizing the Self-Consistent (SC) and Mori–Tanaka (MT) homogenization models, which take into account the contribution of both solid phase and pore structure of the C–S–H. The accuracy of estimates is verified by the data obtained directly from the nanoindentation experiments conducted on the C–S–H gel (e.g., [27,42,11,12,74,29,67]). The outcome of this study provides reliable atomistic models, which are critical to investigate the mechanical behavior of the major constituents of cement-based materials at different scales.

2. Constituents of hydrated cement paste

The hydration of cement starts immediately after it is mixed with water. The cement powder typically contains a wide range of components, each of which with different impurities and reaction rates. Concerning Portland cement for example, these components include dicalcium silicate (C₂S or Belite), tricalcium silicate (C₃S or Alite), tricalcium aluminate (C₃A or Celite), and aluminoferrite (C₄AF or Ferrite). In cement-based materials, the cement components get involved in different chemical reactions during the hydration process and as a result, various HCP products are formed. Due to the complexity of hydration reactions, the nanostructure of the HCP has not been fully characterized yet. However, there are a series of crystalline phases with similar characteristics that can be used to investigate the main chemical and physical properties of the HCP. This section provides an overview of the main HCP crystals used in the current study to calculate the elastic properties of the HCP constituents.

2.1. C–S–H gel

The C–S–H gel has the largest volume contribution to the hydrated cement pastes and is, thus, the main phase responsible for the mechanical properties. The C–S–H gel, which is the result of reactions between the silicate phases of cement and water, can be considered as an amorphous material with variable stoichiometry (i.e., C_aS_bH_c). Investigation of the microstructure of the C–S–H dates back to the beginning of the twentieth century, when Michaelis [41] introduced the colloidal nature of C–S–H. The first model that systematically studied the formation of the C–S–H products was the colloidal model proposed by Powers and Brown-yard [52]. This model considered the hydration reaction products as colloidal structures and called them “cement gel”. Feldman and Sereda [19] later proposed the layered model for the C–S–H with the assumption that the C–S–H solid particles are composed of non-ordered layers that tend to group together. Based on the colloidal and layered models, a hybrid model was developed by Jennings [28]. In this model, which was called CM-I, the solid particles were considered as spherical building blocks that form bigger structures named “globule”. The level that the globules are packed can be tight or loose, which creates Low Density (LD) or High Density (HD) C–S–H gels, respectively. Jennings [30] proposed the CM-II model as a refinement to the former model. In the new model, while the concept of LD and HD gels is kept, the nature of globules was modified such that the basic building blocks are omitted and, therefore, globules are taken as the basic particles. Although the recent model predicted the nanostructure of the C–S–H very well, it was not able to provide detailed information about the solid particles. As a matter of fact, the atomic structure of the C–S–H is still not entirely clear despite the efforts made by Diamon et al. [17], Yu et al. [72], Allen and Thomas [1], Jennings et al. [29], and Richardson [57] to name a few.

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