Molecular modelling of cementitious materials: current progress and benefits

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Abstract

Developing new sustainable concrete technology has become an urgent need, requiring faster and deeper insights into the fundamental mechanisms driving the cement hydration reactions. Molecular simulations have the potential to provide such understanding since the hydration reaction and the cement chemistry are particularly dominated by mechanisms at the atomic scale. In this letter, we review the application of two major approaches namely classical (including reactive) molecular dynamics simulations and density function theory calculations of cementitious materials. We give an overview of molecular simulations involving the major mineral and hydrate phases.

Keywords: Cement; Molecular dynamics; Density functional theory; Reactive molecular dynamics; Simulations

1 Introduction

Manufacturing and utilization of sustainable cementitious materials is essential for reducing the carbon footprint of the cement industry [1,2]. To this end, fundamental understanding of various cementitious materials and reactions together with practical implementable solutions is the need of the hour. An immediate solution adopted include higher replacement of Portland cement (PC) with less carbon intensive supplementary cementitious materials (SCMs) [3,4] and new types of cements such as limestone calcined clay cements (LC^3) [5]. However, such solutions are still under intensive experimental research requiring a deeper understanding of several mechanisms at the atomic scale which essentially dictate the properties or behavior at the macroscopic scale.

In terms of mineralogy, PC is composed from 50 to 70% of impure tricalcium silicate (alite: C_3S) as main mineral, 15 to 30% of dicalcium silicate (belite: C_2S), 5 to 15% tricalcium aluminate (aluminate: C_3A), and 5 to 10% tetracalcium aluminoferrite (ferrite: C_4AF) and a small amount of gypsum [6]; where C, S, A, and F represent CaO, SiO_2, Al_2O_3, and Fe_2O_3, respectively [7,8]. Upon hydration, cement undergoes a complex multiphase reaction involving dissolution and precipitation of various hydrates such as calcium silicate hydrate (C-S-H), calcium hydroxide (C-H), ettringite,

monosulfate. The nature, extent, and kinetics of these hydration reactions ultimately control the chemical and physical properties of the cementitious materials for short- and long-term performance [9,10]. However, such reaction process is far from fully comprehended regarding the complexity of the chemical interactions, which are difficult to characterize from the experimental point of view, limited both by temporal and spatial resolution. The key mechanisms of such reactions occur in the range of a few nanoseconds and a few nanometers. Gaining knowledge at this scale would enable the cement chemists to ideally control and tailor the cement hydration reactions that will ultimately enable them to make sustainable concrete with tailored properties.

With significant improvements in computing power, nanoscale modeling has emerged in materials science as a promising field of investigation. Atomistic simulation methods (Figure 1) have demonstrated a great potential to expand the fundamental understanding of cementitious materials. Conventional molecular simulation methods such as density functional theory (DFT) are mainly used to explore various static properties as electronic, structural, and mechanical properties of bulk structures. By considering the electronic state of the system, DFT presented a powerful tool to investigate the chemical reactions occurring at the early ages during the hydration of unhydrated phases.

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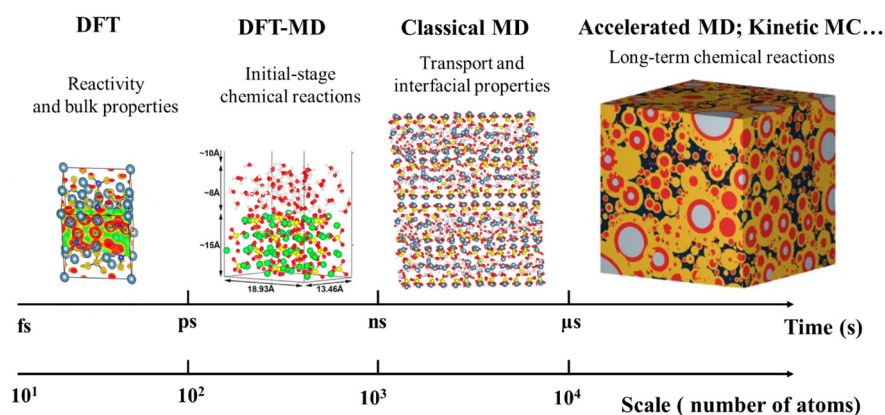
Figure 1. Schematic of atomistic simulation methods in various time and space scales.

On the other hand, classical molecular dynamics (MD) [11], based on the Newton's equations of motion, could simulate a large box (with dimensions of a few tens to hundreds of nanometers in each direction) of atoms (from hundreds to millions of atoms) over extended periods (up to a few nanoseconds), and applied to elucidate the microscopic mechanism of cement hydration and transport properties. In this method, the interactions of the atoms are captured using a set of empirical potentials known as force fields. A review of the force fields (FF) applied to simulate cementitious materials has recently been published [12]. An interesting one, would be a reactive force field (ReaxFF) [13,14], which can qualitatively describe the forming/breaking of chemical bonds, and thus is useful for analyzing chemical reactions in rather large systems beyond the scope of DFT (typically limited to a few hundreds of atoms and a few picoseconds). Such methods are considered as powerful tools to simulate experiments that could not be carried out in laboratory because of their high cost or technological limitations.

Recently, many studies have been conducted regarding atomistic simulations to investigate the cement phases to predict and explain the microscopic physical and chemical properties. In this letter, we discuss some of the works that have utilized such computational methods to gain better insights into cementitious materials. The three main topics that are of much interest to cement chemists from the atomistic point of view are:

(1) Hydrated and unhydrated bulk structures
(2) Interaction at interfaces
(3) Interaction of species in pore solution

In addition, the connection between nano-scale and macro-scale will be also discussed, with the focus on what could be learned from molecular simulation to predict the macroscale behavior and gain much needed insights to develop new cement-based materials with tailored properties.

2 Simulations of bulk structures

Bulk simulations are done either on a unit cell in the case of DFT or on supercells (unit cells repeated in the different crystallographic directions more than once) in the case of classical MD simulations. There are different properties that

one can calculate from such calculations. They also serve as a benchmark for the simulations or drawing benchmarks on the error or deviations that can be expected with the simulations. In the context of cementitious materials, simulations of bulk structures are an experiment of its own, especially in the case of nanocrystalline C-S-H.

2.1 Mineral phases

The four clinker phases were intensely investigated theoretically and experimentally, in particular the alite and belite polymorphs [15–38]. In the following sub sections, we review the papers based on the type of properties or insights that were investigated.

### 2.1.1 Structural, mechanical and thermal properties

The molecular simulation approach is considered as a powerful technique that can be used to identify and quantify the bulk properties such as the structural and mechanical properties of cement mineral phases. These properties serve as a validation for the simulations, the choice of pseudopotentials for DFT and FF for MD, as they form the basis of whether the simulated structure represents the actual behavior of the solid material. In this review, we do not cover these properties in detail as these are much well discussed in many of the recent reviews and papers published [15–38].

In addition, the thermal properties such as heat capacities and thermal conductivities are also calculated for $M3$-C_3S and C_2S together with C-H and C-S-H [39]. Using a homogenization scheme the authors then were able to compare it to a hydrated C_3S paste. Recently with two different force fields, the heat capacities, thermal conductivity and thermal expansion coefficients of T1 and M3 polymorphs are calculated and are found to be consistent with the earlier simulations.

2.1.2 General reactivity

Based on DFT approaches, the electronic properties and reactive sites are predicted in bulk minerals. Laanaiya *et al.* revealed two oxygen atom-types from charge density analysis in alite crystal structure (Figure 2a) [19]. Then, Local density of

states (LDOS) of valence band maximum (VBM) and conduction band minimum (CBM) were performed to characterize reactive site.
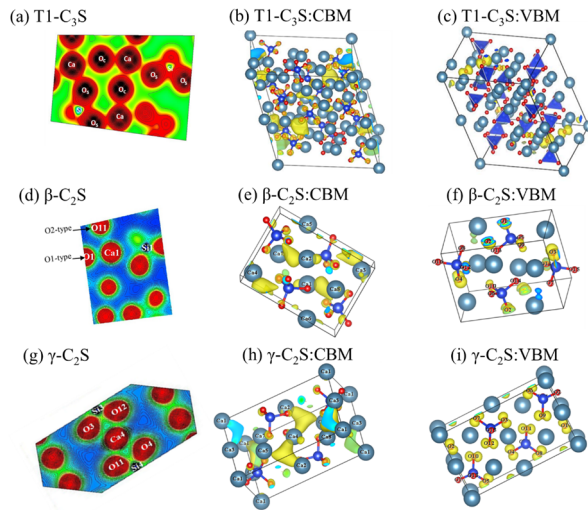
Figure 2. Charge density distribution and LDOS of VBM and CBM respectively for: (a) (b) and (c) T1-C3S; (d), (e) and (f) β-C2S; (g), (h) and (i) γ-C2S. Atomic color codes are oxygen: red, calcium: tourqois, silicon: blue [19,23]. Copyright 2019, 2021 Elsevier.

The results show that the calcium atoms are susceptible to be active under nucleophilic attack such as OH⁻ (Figure 2b). The reactivity under electrophilic attacks such as H⁺ is mainly due to oxygen atoms which are only bonded with calcium atoms, while the oxygen atoms bonded to silicone atoms in SiO_4^{4-} tetrahedrons are expected to be inactive (Figure 2c) [19]. Similarly, two types of oxygen atoms were distinguished in β-C_2S (Figure 2d); whereas γ-C_2S exhibits a high symmetry in the charge distribution over all oxygen atoms (Figure 2g). The highly located LDOS of VBM around one oxygen type atoms in β-C_2S indicates high reactivity under electrophilic attacks (Figure 2e), while the uniformly distributed LDOS of VBM could explain the non-reactivity to water of γ-C_2S (Figure 2i) [23]. Such theoretical works attempted to introduce impurities to enhance the β-C_2S reactivity rate with water [23,40]. Furthermore, DFT studies reported that C_3A reactivity originates from O-2p, Ca-3p, Ca-3s and Al-3p orbitals, and that the LDOS of the VBM and the CBM are localized in the vicinity of oxygen atoms and calcium atoms respectively [41]. However, for brownmillerite, the major constituent of C_4AF,

the LDOS of the VBM is localized at the vicinity of oxygen atoms, while the LDOS of the CBM is mainly localized on Fe atoms [42,43]. These studies suggested that oxygen atoms in the Fe octahedral plane would be the most likely to suffer electrophilic attack [42,43].

2.1.3 Incorporation of minor elements

The major elements that are investigated for incorporation in C_3S are Al, Fe, Mg, Zn and Cu [44–49]. Using a combination of MD and DFT approaches, Manzano *et al.* investigated Al, Fe and Mg incorporation in M3 polymorph of C_3S [44]. The authors substituted Ca^{2+} sites with Mg^{2+}, while a Ca^{2+} + Si^{4+} species was substituted with two times Al^{3+} or Fe^{3+}. From the lattice energies calculated, there was no preference for any site and the substitution did not have a significant effect on the indentation modulus calculated. From the visualization of changes in the VBM and CBM, Al^{3+} slightly reduced the reactivity, while Mg^{2+} did not make any considerable changes. In the case of Fe^{3+}, a considerable localization was observed indicating a reduced reactivity (Figure 3). The authors inferred that this difference might induce a noticeable decrease on the dissolution rate with respect to the pure or the Mg and Al substituted alite and belite. A larger number of elements (Mg, Zn, Ba, Cu, Al, Fe, Ga) were looked at recently by Wang *et al.* [48] for possible substitutions in M3 and M1 polymorphs of C_3S. Another interesting set of elements are Zn and Cu [50–52], as they are known to affect the hydration kinetics when present in the clinker. Interestingly, some studies acknowledged the fact that reactivity of the system might be solely dependent on surface electronic structure rather than the bulk [44,53]. In addition, surface roughness, grain boundaries, defects, phase segregation etc. might also dominate the reactivity [54,55].

2.2 Hydrates

Hydration of alite dominates the main hydration peak observed by isothermal calorimetry. When alite reacts with water the reaction products are calcium silicate hydrate (C-S-H) and portlandite (CH). The aluminate phases react to form ettringite and monosulfate depending on the availability of gypsum. C-S-H the main hydration phase is a nanocrystalline or noncrystalline material, i.e., there is no long-range order and has been the subject of several atomistic simulation investigations since deciphering its atomic structure has been incredibly challenging on the experimental front [56–59].
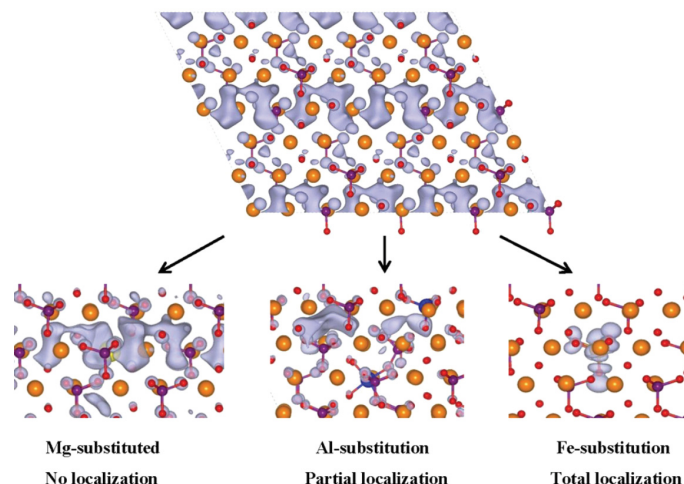
Figure 3. VBM distribution on pure alite unit cell and details of the localization for Mg, Al and Fe chemical substitutions. Atomic color codes are oxygen: red, calcium: orange, silicon: purple, magnesium: yellow, aluminum: blue [44]. Copyright 2011 American Chemical Society.
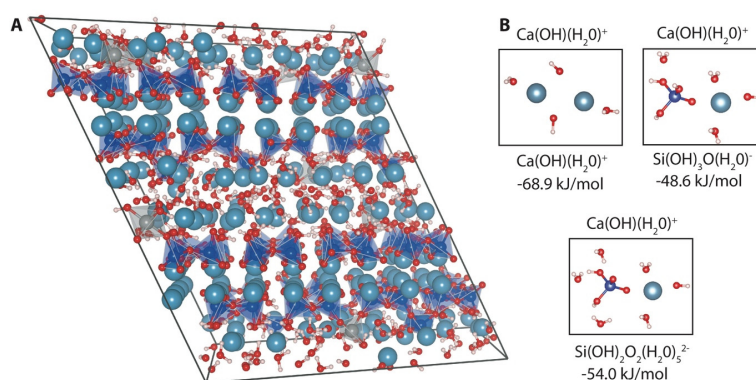
Figure 4. A bulk atomic-level structure of aluminum incorporated C-S-H is shown in (A), taken from [73], copyright 2020 American Chemical Society. Free energy of complexation of a few early age hydration species in solution are shown in (B), adapted from [79]. Atomic color codes are oxygen: red, hydrogen: white, calcium: tourqois, silicon: blue, aluminum: grey.

2.2.1   C-S-H atomistic models

C-S-H has a layered structure with the atomic structural features similar to the ones in the tobermorite family and is known to be a defective tobermorite structure at the atomic-level [57,60–62]. It was Pellenq et al. [81] in 2009 who first employed molecular dynamics modeling to develop the first disordered C-S-H full atomistic model based on the tobermorite 11Å structure. While the model reached some agreement with selected experimental data, it was criticized due to inconsistent densities and especially the local bonding environment of calcium [88, 89]. This was followed by an improved combinatorial approach later addressing those shortcomings and using the ReaxFF force field [63]. Another attempt was from Kovačević et al. which essentially showed that the different energies of the final structure will depend on the way the defects in tobermorite structure are made [64]. Both approaches used MD as a large supercell is necessary to capture the different defects or features of C-S-H. This was followed by the brick model of C-S-H which allows precise control over the type and location of defects in three-dimensional structure of C-S-H [65]. It can be viewed as a bottom-up approach with inputs from experimental

characterization of high Ca/Si ratio synthetic C-S-H. A more detailed discussion on the different C-S-H models, their limitations and advantages have been recently published [66] and is beyond the scope of this paper.

2.2.2   Application of C-S-H models

The above-mentioned C-S-H models and their variants have been used to calculate mechanical properties, chemical shifts, structure, and dynamics of water or other ions within C-S-H interlayer or in the pores [67–75]. Although some of these calculations are insightful, it is often difficult to match with the experimental observations due to the inherent complexity of the multiscale features of C-S-H. Another application of these models was to investigate the nature and location of aluminum in C-S-H. Manzano et al. used DFT approach to find that aluminum preferentially occupies the bridging site of a simple isolated linear silicate chain in a four-fold coordination [76]. This was later confirmed in the full C-S-H models using both DFT and classical MD [71,77]. Recently, Kunhi Mohamed et al. using the brick model and experimental NMR measurements showed that aluminum can exist both in four-fold and six-fold coordination geometries in C-A-S-H at the same bridging site (Figure 4a) [73]. The authors also

calculated NMR chemical shifts of aluminum and silicon atoms using GIPAW approach based on DFT calculations and thus were able to show the non-existence of a third aluminate hydrate (TAH) proposed to explain the six-fold coordinated aluminum in C-S-H. Essentially, all these works show that atomistic simulation methods are found to be extremely useful in deciphering the nanostructure of C-S-H. Furthermore, the structural information from the brick model of C-S-H has been used for a new CASH+ sublattice solid solution model in the GEMS thermodynamic modeling software [78].

2.2.3   Other hydrates

The first molecular simulation on the bulk properties of ettringite was carried out by Manzano *et al.* [80]. Further studies include both DFT [81,82] and MD approaches [83–86]. Honorio *et al.* developed a new force field named AFFF for ettringite, monosulfoaluminate and C_3A [84]. The validated force field was further employed to investigate the sorption behavior of ettringite using MD and grand canonical Monte Carlo simulations and thermal properties of ettringite [87,88].

3   Simulations of solid-water interfaces

At the early ages of hydration, the cement reactions are facilitated through the interactions at the solid-liquid interfaces. At later ages, this is then replaced with the many connecting pores which provide the required solid-liquid interfaces for ion transport and continued chemical reactions that affect durability. Admixtures also act primarily at such interfaces to modify the kinetics of the chemical reactions and/or change the rheological properties.

3.1   Mineral phases

A mineral-water interface would consist of one of the crystallographic surface cuts of the mineral in contact with a simulation box containing water and any ions or molecules of interest.

3.1.1   Reactive sites and adsorption of water molecule on mineral surfaces

Modeling the surface of a mineral can help to identify the most reactive regions. This can be achieved by finding the minimum energy configuration of the system and calculating the adsorption energy of water molecules at different location. DFT and ReaxFF simulations were performed to depict the adsorption of water molecules on M3-C_3S, γ-C_2S and β-C_2S surfaces [36,89,90]. DFT calculations showed that the adsorption energies are lower for the dissociative adsorption than for molecular adsorption, suggesting a higher probability for the former to occur [89]. Nonetheless, Zhang *et al.* showed that the adsorption mode in M3-C_3S depends

clearly on the number of adsorbed water molecules [91]. In addition, simulations of water adsorption on different β-C_2S surfaces were performed. Interestingly, the authors did not find a correlation between the electronic structure and the adsorption energies despite the elucidation of the adsorption mechanism [92]. In addition, Wang *et al.* suggested that the larger reactivity of β-C_2S compared to the γ polymorph may be due to its lower symmetry [36]. The influence of impurity on the water adsorption on β-C_2S and M3-C_3S was also investigated [93,94]. DFT-MD simulation showed that Cu-doping influenced the electronic structure of β-C_2S, promoting the dissociation adsorption on the surface around Cu atoms and weakening the chemical bonds   with the water namely the calcium- oxygen (water) bond and hydrogen (water)- oxygen (from the silicates tetrahedra) [92]. Mg impurities resulted in a formation energy unfavorable and did not significantly affect the frequency of water dissociation [94].

3.1.2   Early-age hydration reaction

The hydration process is one of the most complex phenomena and is far from fully comprehended regarding the complexity of the successive chemical interactions. It involves various complex phenomena as dissolution, diffusion, nucleation, and growth. The molecular simulations (MD and DFT) were performed to elucidate the early age of this complex process. Using ReaxFF-MD simulations, Manzano *et al.* predicted two hydration mechanisms for M3-C_3S depending on the hydrated surfaces (Figure 5) [95]. On (001) M3-C_3S, a tessellation process was observed, where a stable monolayer was formed inhibiting the continuation of the hydration process. On other M3-C_3S surfaces, the hydration mechanism was described as "reaction and hopping" process [95]. Such process induced a diffusion of protons inside the bulk, then a desorption of calcium atoms and a rearrangement of silicate tetrahedrons, which may lead to their oligomerization [96]. Similar process was found for hydration of γ-C_2S and β-C_2S [36]. Wang *et al.* reported that water dissociates faster on γ-C_2S, yet the reactions slow as the few reactive sites are saturated, while β-C_2S kept on reacting for a longer time since the surface has more reactive points [36]. Other studies pointed out the influence of the mineral surfaces on the reactivity process by examining the effect of the surface dissimilarity between C_3S-C_2S and the effect of different surface impurities [93,97,98]. In addition, C_3A and gypsum interfaces were also investigated with a thin layer of water using ReaxFF force field by analyzing the adsorption configuration, penetration depth, diffusion distance, and the radial distribution function [99].
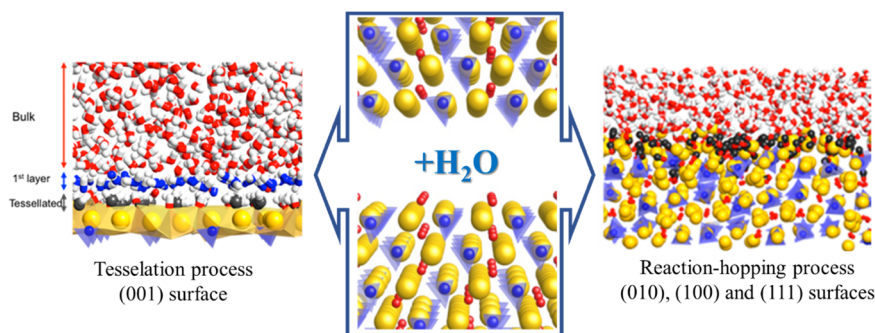
Figure 5. Different mechanism process of M3-C3S hydration depending on the hydrated surface. The hydrogen atoms from dissociated water molecules are represented in black to illustrate their absorption within the mineral structure. In tesselation process, the oxygen atoms of water molecule in stable monolayer are in grey, of the fist adsorbed layer are in blue light. Other atomic color codes are oxygen: red, calcium: yellow, silicon: blue, hydrogen: white, adapted from [95]. Copyright 2015 American Chemical Society.

Based on conventional molecular methods, Pustovgar *et al.* modelled the hydrating surface of C_3S by proposing a sequence of hydroxylated C_3S state depending on the pH [20]. Recently, by combining DFT-MD and metadynamics [100] simulations, the dissolution mechanism of Ca ions from C_3S surface was investigated [101]. The calcium sites with different coordination environments lead to different reaction pathways and free energy barriers. As a result, the detachment of low-coordinated Ca species was spontaneous and easier to leach from surface, while high-coordinated Ca results a non-spontaneous one [101].

3.1.3 Long-term hydration process: Limitation of conventional molecular simulation

The hydration process is considered as a large-scale chemical reaction process with complex multiphase chemical reaction systems. While, due to the limitation of timescale, the conventional molecular dynamics simulations discussed here cannot describe the whole hydration process. By leveraging transition state theory and bypassing fast dynamic events occurring within the same metabasin in the energy landscape, the kinetic Monte Carlo (KMC) can predict the evolution of a surface for longer hydration times [102]. However, such method could not elucidate the entire dynamical evolution of the system because only specific events (i.e., jumps over energy barriers) are considered. As promising method, RedMoon which is a hybrid method combining MC and MD methods that can treat the reaction process as a stochastic process and capable of simulating a large-scale chemical reaction. So far, this new atomistic reaction simulation has shown great applicability to reproduce the heterogeneous atomic structures [103–105].

3.2 Hydrates

3.2.1 C-S-H interface

Although C-S-H bulk structure is well researched upon and understood, its surface is still somewhat of a mystery. It is known that C-S-H has a high specific surface area (between 200 and 300 m^2/g [106]), which underlines the importance of C-S-H surface in the process of cement hydration [9] with many dynamic interactions of the dissolving ionic species. Such interactions dictate the cement or concrete microstructure development, thereby influencing the long-term durability and other properties of the concrete structure. Nowadays, most of the C-S-H surfaces simulated are either (001) surface of non-defective tobermorite [107] or in a few cases, random defects are created on this surface [107] or the interlayer of a C-S-H model is treated as the surface in contact with the pore solution [108]. This is mainly due to the fact that, we still do not know the exact features of the surface either from experimental or theoretical works. So far, the features on the surfaces are randomly (or followed by some notion of negative surface) used. In most cases if the bridging silicates are removed, they are not replaced by calcium atoms, which should be the case in the C-S-H structure [74]. At high 'real system' Ca/Si ratios, around 75% of the bridging sites are missing [74]. While silicates get deprotonated at pHs in which C-S-H exists, they give rise to negatively charged surfaces. When bridging silicates are replaced by calcium ions, calcium compensates for the negative charge of the deprotonated silanol groups, making the local surface charge neutral. Therefore, a realistic C-S-H surface would appear less negatively charged as assumed in previous studies, or in other words, the surface chemistry would depend on the solution condition and is still a subject of further research.

3.2.2 Other hydrates

Among the other hydrates, portlandite (CH) is simulated with classical force fields with the Buckingham based potentials [109,110] or Lennard-Jones based potentials [111]. Using metadynamics method, Galmarini *et al.* calculated the adsorption energies of calcium ion, hydroxyl ion, silicate ion and a calcium silicate complex on different surfaces of portlandite [109,110]. The authors were able to relate their results to the crystal growth mechanisms observed experimentally. Recently, Mutisya et al. used metadynamics and AIMD to explore the interaction of CO_2 on CH surfaces [112]. Other than this, not many simulations are done on portlandite although it remains an important part of Portland cement and remains essential for the pozzolanic reactivity in new low clinker cements[5] and other new research avenues [113,114].

Kalinichev *et al.* simulated chloride binding on CH, ettringite, tobermorite and Friedel's salt using the CLAYFF force field [111]. Recently, Hajilar *et al.* simulated with varying

concentrations of sodium and chloride ions on (100) ettringite surface using the same force field [115]. Tararushkin *et al.* employed an improved CLAYFF force field [116] with metal-O-H bending angles and captured the elastic properties of ettringite better [86]. With this force field, the authors also simulated the structure and dynamics of sodium, sulfate and chloride ions with a (100) surface of ettringite. So far, there are no interfacial simulations using AFFF [84] reported.

4 Simulations of pore solution

During the early hydration period, the dissolved ions undergo a serios of steps involving formation of complexes, clusters, nuclei and then eventual growth into crystalline or amorphous or nanocrystalline materials. Atomistic simulations with some multiscale modeling could explore this domain much better. Currently, only a few studies on the very early age complex formations have been investigated. Galmarini *et al.* using enhanced sampling methods investigated the existence and stability of a calcium silicate complex that might play an important role in early C-S-H formation [110]. Using ReaxFF MD, Du *et al.* simulated the polymerization rate of different Ca/Si ratio solutions [117]. Yang and White modeled the interaction of different species during the early age hydration period using DFT [79]. The authors used an implicit solvent enabling them to simulate a high pH solution and calculated the free energy of complexation. With these values, the authors were able to propose possible formation pathways for C-A-S-H gel. The authors highlighted the limitations of this study in terms of only looking at monomeric species, however, this was first of its kind and the first step towards understanding the formation pathway of C-A-S-H (Figure B). Recently, Aretxabaleta *et al.* used a combination of several different techniques to assess a possible C-S-H nucleation pathway from a monolayer of portlandite [118]. The authors concluded that although such a mechanism is possible, one must consider the formation of calcium silicate complexes which could prevent the formation of the portlandite monolayer in the first place. However, such advanced simulations together with experiments are paving the way for deeper understanding of cementitious systems.

5 Conclusion and Outlook

In this review, the recent advances in the molecular modeling of cementitious materials are presented and discussed. For more in-depth discussion, there are several review papers recently published on some of the topics discussed here [66,96,119–121]. Many of the simulations that have been done so far are primarily, in our view, more of validation or comparison of structural and mechanical properties. Molecular simulations can usefully verify experiments, but it has matured to even explain the mechanisms underlying the experimental observations and get insights into specific questions. Cement hydration reaction and other transport related mechanisms affecting its durability are indeed governed by mechanisms at the atomic level. As such, molecular modeling techniques have immense application in these systems. However, unlike other fields such as semiconductors, the phases in cementitious systems which

are produced at large scale from local raw materials are found to be associated with varying amounts of defects, impurities and minor elements. Hence, care must be taken in interpreting results and comparing to experiments. Often, molecular modeling works best when the scientific question can somehow be related to the molecular level. As discussed here, the methods and computational resources have significantly improved over the years to treat such molecular simulations as lab experiments.

As for bulk reactivity of mineral phases, DFT simulations were mainly performed to characterize the reactive sites in the bulk structures. Although such studies give an insight into the origins of the reactivities of these minerals, the kinetics aspect of the reactivity during the hydration reaction is not essentially captured. Within this limitation, these studies provide us the much-needed fundamental understanding of how the impurities or dopants could potentially affect the intrinsic bulk reactivity of the mineral phases. Together with MD methods, various complex phenomena could be investigated such as nucleation, dissolution and diffusion. Furthermore, diverse MD-based methods were employed to depict the adsorption of water molecules on the cementitious mineral surfaces and elucidate their microscopic mechanism in the early-age hydration process. Yet, the interpretation of these simulation results should consider the limitations, principally, of the time scale or the kinetics.

In the case of C-S-H, simulations have played a major role in our understanding of the material. With the use of new types of cements, such amorphous or nanocrystalline or crystalline products formed can be better characterized using molecular simulations. Dynamics of water on mineral surfaces are interestingly explored, but progress in terms of advanced molecular methodologies is still required to reduce the gap between simulation and experimentation results [122]. However, in the case of hydrates and nanometric pore channels, MD has the advantage over the experiments. Although experimental characterization is challenging, a proper validated simulation could also give insightful details into the phenomena or mechanisms that can be tested. Much of the focus has been on the C_3S or to certain extent on tobermorite/C-S-H interfaces, the other hydrates are still to be explored provided there are sound questions to be addressed.

With the recent developments and widespread use of enhanced sampling techniques coupled with DFT and MD, the future of molecular simulations in the field of cementitious materials is promising [104,118,119]. These techniques enable wider exploration of the system essentially overcoming the limitations of time and energy barrier constraints in the normal MD or DFT simulations. The development of more accurate and computationally efficient machine-learned forcefields also has the potential to bridge the gap between classical MD and DFT [123,124]. With the urgent need to develop sustainable solutions for new cement and concrete technologies, such simulations can give a first-hand direct insight into the mechanisms of new cement formulations. This would enable the cement chemists a knowledge driven development of new technologies.

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Authorship statement (CRediT)

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Amine Bouibes: Conceptualization, writing - original draft, review and editing

Mathieu Bauchy: Writing - review and editing

Ziga Casar: Writing - original draft, review and editing

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