

Review

A Review: Progress in Molecular Dynamics Simulation of Portland Cement (Geopolymer)—Based Composites and the Interface between These Matrices and Reinforced Material

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Abstract: Molecular dynamics (MD) is an important method for studying the molecular and atomic scale of cement (geopolymer)-based composites which provides an effective method for the optimal design of cementitious materials. In this paper, the research progress of MD simulation in Portland cement and geopolymer-based materials is discussed in detail, including molecular structure models of calcium silicate hydrate, calcium aluminosilicate hydrate, sodium aluminum silicate hydrate gel, and auxiliary experimental techniques. The basic mechanical properties of calcium silicate hydrate, calcium aluminosilicate hydrate and sodium aluminum silicate hydrate in Portland cement-based materials (CBM) and geopolymer-based materials are reviewed. In addition, the dynamic simulation of the interface between CBM and reinforcement materials such as rebar, synthetic fibers, plant fibers and nanoparticles is also discussed. Through the macroscopic experimental results of cement (geopolymer)-based materials and the performance analysis of an MD microscopic model, MD helps to better explain the macroscopic properties of materials, and can quickly and conveniently analyze the mechanical properties, transport properties and interface properties of composite materials, so as to improve the fine design of cement (geopolymer)-based materials. Existing structural models and force fields are affected by environment and time, and MD simulation shows great differences in application range and characterization ability. It is necessary to further study and reveal the internal mechanism for improving concrete performance through a large number of experiments and MD simulation, and lay a theoretical foundation for preparing the next generation of (super) high-performance concrete.



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1. Introduction

Concrete has been widely used because of its high compressive strength, strong corrosion resistance, high durability, high cost–performance ratio, and simple production process. At present, more and more in-depth research on concrete materials has been carried out, and the requirements for its mechanical properties have become higher and higher. The only disadvantage of compressive strength is that it cannot meet the requirements of engineering practice. The research into high-strength, high-ductility, and high-durability concrete materials has become one of the current research hotspots. It is the most important means for improving the performance of concrete, by introducing reinforcements such as steel bars, fibers, nanoparticles, etc. However, whether the reinforcement can

effectively enhance the properties of concrete depends on the bonding performance of the reinforcement/matrix interface.

Concrete has significant multiscale characteristics. At the macroscale ($>10^{-3}$ m), concrete consists of cement paste and aggregate. At the mesoscale (10^{-6} – 10^{-3} m), hydrated calcium silicate gel and other products of hydration form the heterogeneity of cement-based materials (CBM). At the microscale (10^{-9} – 10^{-6} m), it can be considered that hydrated calcium silicate gel is formed by the accumulation of hydrated calcium silicate particles of various dimensions and densities. At the nanoscale ($<10^{-9}$ m), calcium ions, silica-oxygen tetrahedrons, and water molecules form together the most basic unit of hydrated calcium silicate gel.

The main binder of conventional concrete is Portland cement, and its main hydration product is hydrated calcium silicate, which is the bonding phase in the cement concrete material. It is also the source of strength of cement concrete materials, and affects the main mechanical properties (MPs) of concrete materials. XRD, DTA and chemical analysis were used initially to obtain the average components of hydrated calcium silicate. In the mid-twentieth century, electron diffraction and electron microscopy were used to determine by mole the molecular structure of hydrated calcium silicate. Taylor found that the main product of Portland cement reaction with water is hydrated calcium silicate gel, and his ideas provided an important foundation for the research into hydrated calcium silicate [1]. However, as low-carbon, green development has become a global concern, geopolymers are regarded as an important alternative gelling material to Portland cement. This is because the geopolymers are low-carbon and low-energy, and can consume bulk solid waste such as fly ash, slag, silica fume, etc. Geopolymers differ as to whether sodium aluminosilicate hydrate gel or calcium silicoaluminate hydrate is the primary gel, depending on the raw materials [2].

In the late 20th century, computer performance was greatly improved and people started to study the structure and the performance of hydrated calcium silicate, using computers, at the atomic level [3]. MD simulation is a false method of studying simulated objects. In MD simulations, the atoms in the system are abstracted as particles, and the interaction between the atoms is described by a potential function. Numerical methods are applied to obtain the trajectories and velocities of the atoms in phase space. Then the statistical theory is applied to research the thermodynamics and MP of the whole system. Compared with macroscopic theoretical analysis and experimental studies, the study of hydrated calcium silicate composition at the nanoscale using MD simulations reduces a great many complicated and tedious theoretical derivations and experimental costs. In addition, it studies the internal characteristics of hydrated calcium silicate in depth from a microscopic perspective and obtains some results that cannot be obtained by theory and experiments. In recent years, as geopolymers have become a research hotspot, MD simulations on the main gel phase of geopolymers have also gained the attention of relevant researchers. MD simulation methods have been used to model and illustrate gels in cement-based materials [4,5], ion migration [6,7], and nanoscale mechanical behavior [8,9].

Researchers have carried out a lot of study on the preparation and macroscopic properties of cement (geopolymer)-based materials, and have achieved fruitful results, but there are still great limitations in the study of microstructure, and the reaction mechanism and action law of its microstructure are not clear. And, continuing with qualitative research, there is a lack of systematic theoretical research. In addition, since the properties of all aspects of the material are controlled by its microstructure, the relationship between the microstructure and macroscopic properties of cement(geopolymer)-based materials is not clear, due to the complexity of hydration or polymerization reactions, so it is of great significance to study and characterize the microstructure of cement-based materials using the molecular dynamics system. Similarly, the study of the interfacial properties of steel bars, fibers, and nanoparticles with cement(geopolymer)-based materials through molecular dynamics is also helpful for improving the design level of cement (geopolymer)-based composites, and also lays a theoretical foundation for further optimization and improvement of (super)

high-performance concrete properties. Therefore, in line with the research achievements in recent years, this paper introduces the theoretical basis, common models, macroscopic experimental methods, force field characteristics, MD research achievements and existing problems of materials and their interfaces into the study of cement (geopolymer)-based materials. Finally, the application prospect of MD simulation in the study of cement (geopolymer)-based materials is prospected.

2. Overview of Molecular Dynamics

Since the end of the twentieth century, with the development of computers, numerical simulation calculations, a research method, has started to emerge, which compensates for the huge cost of experiments and the tediousness of theoretical derivations. The number of people studying materials has also been shrinking, and exploration from the macroscopic world to the microscopic world has continued. The methods of simulation studies have evolved from macroscopic finite element simulation to microscopic molecular simulation, and then to nanoscopic molecular dynamics simulation and first principles. The calculation scale has continued to shrink, from the macroscopic centimeter level to the micro nanoscale level. Molecular simulation is essential for modeling and simulating calculations of micro- and nanomechanics [10].

Based on the classical mechanical model of the atomic systems, molecular simulation studies the structure and properties of substances from the atomic level through computer simulation technology, including molecular mechanics, MD simulation, discrete particle dynamics simulation, etc. [11]. The basic idea and method of MD simulation are as follows: treating atoms as particles and taking them as basic elements, the controlling equation is Newton's second law, and using computer technology, selecting suitable empirical potential functions, the process of dynamic change of molecules in the whole material system with time is derived through simulation, and then the macroscopic properties of the system are obtained through the method of thermodynamic statistics. In recent years, with the theoretical methods and the updating of computer technology, MD simulation has been a useful method for exploring materials science.

MD simulation is a modeling research tool through which we can observe not only the microstructure of atoms, but also the dynamic evolution of the whole molecular system, through the results of simulation calculations. First principles, MC, and finite elements (FEA) are three typical computational methods in computational materials science, in addition to MD simulations. Figures 1 and 2 show the computational flow and working frames of the molecular dynamics simulation [11].

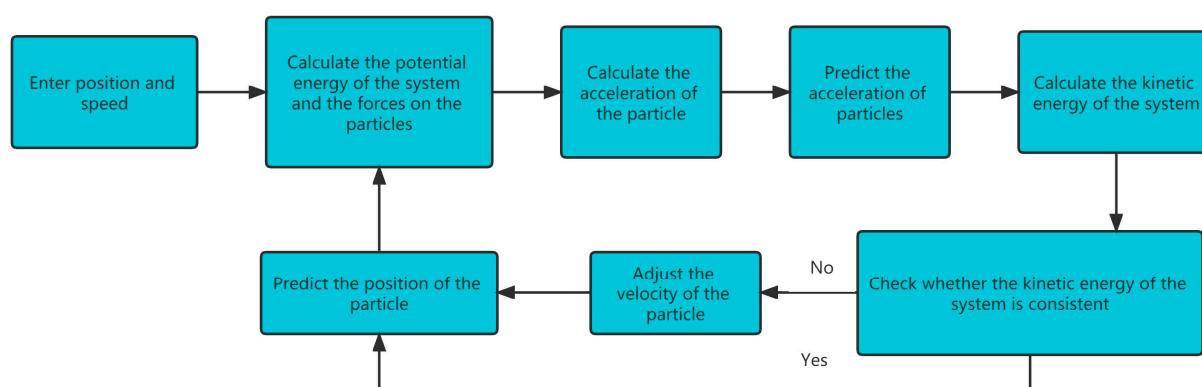


Figure 1. Computational flow of MD simulation.

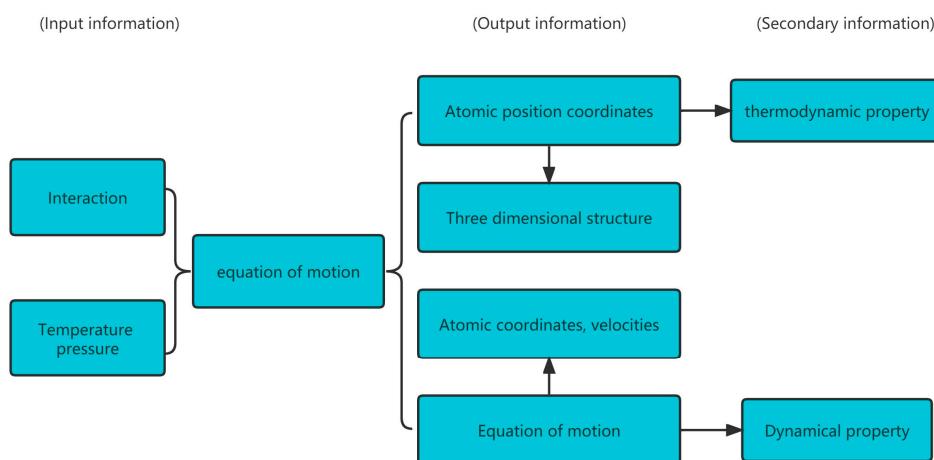


Figure 2. MD working simulation block diagram.

Calcium silicate hydrate is the main product of cement hydration, and its basic composition is SiO_2 , CaO and H_2O [12]. However, calcium silicate hydrate has a wide range of chemical compositions and no fixed spatial structure. The chemical composition of calcium silicate hydrate is characterized mainly through the calcium–silicon ratio (Ca/Si) and water–silicon ratio (H/Si). However, its chemical composition is greatly affected by the ambient temperature and hydration time. Based on modern testing and analysis techniques, many scholars have carried out research on the structure, durability and mechanical properties of calcium silicate hydrate. Okada et al. [13] synthesized hydrated calcium silicate with different Ca/Si ratios, using the hydrothermal method, and used ^{29}Si nuclear magnetic resonance to explore the effects of Ca/Si and synthesis temperature on the silicon chain structure. Chang Jun et al. [14] synthesized hydrated calcium silicate with different Ca/Si ratios using the chemical co-deposition method, and discussed the effect of Ca/Si on the carbonization rate of hydrated calcium silicate. Although these analytical and testing techniques have played a certain role in promoting the research into calcium silicate hydrate, the research into calcium silicate hydrate is not comprehensive, due to the limitations of the accuracy of the test instruments and the purity of materials. In recent years, the development trend in materials research has gradually changed from macro to micro. Molecular dynamics simulation has become a powerful tool for studying the microstructure of materials, and has played an important role in the characterization test of materials. By comparing the simulation results obtained from molecular dynamics simulations with those from the mechanical field of macroscopic experiments, researchers have made great efforts to obtain accurate molecular models of the structural characteristics of calcium silicate hydrate and obtain greater value from cement-based materials.

With the development of technology, the micro-level calculation has become an important technique for studying the MP of structural materials. Among these methods, MD simulation has made significant developments in many fields, due to its ability to discover the basic principles of reactions and interactions, and to assist in the selection and design of materials. In this paper, the number of papers on the MD model published in SCI journals from 2012 to 2021 and the number of papers on cement-based MD are counted, as shown in statistical Figure 3. We can see from the table that the number of papers on cement-based materials based on MD has shown a significant upward trend, and has gradually become a research hotspot.

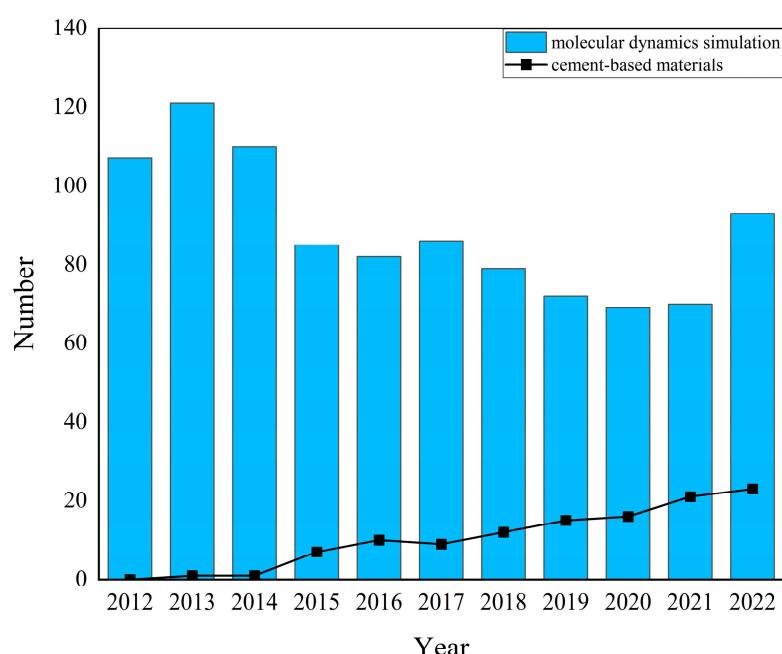


Figure 3. Number of SCI-searchable papers on MD simulation and cement-based materials.

3. Molecular Structure Model of Cement (Geopolymer) Gel

3.1. Molecular Structure Model of Hydrated Calcium Silicate Gel

The morphology of hydrated calcium silicate gels is more complex and variable, ranging from fibrous crystals to reticulated amorphous forms. Because they exhibit a colloidal scale and a tendency to cluster, hydrated calcium silicate gels can only be distinguished by electron microscope, and their true internal crystal structure has not been specifically determined yet. Insight into the composition of hydrated calcium silicate gels and the corresponding structural model features is important for understanding, regulating, and controlling the MP and chemical stability of cementitious composites.

The reaction of $\text{Ca}_3\text{O}_5\text{Si}$ and $\text{Ca}_2\text{H}_4\text{O}_4\text{Si}$ in Portland cement with water forms a series of hydrated calcium silicate gels. The structures of these hydrated calcium silicate gels are similar, but the ratio of Ca to Si and the content of chemically bound water are significantly different [15]. Since the structure of a substance is an important factor in determining its properties, the different ratios of the elements within hydrated calcium silicate gels can lead to obvious differences in their physical properties. With the continuous development of micro- and nanomaterial processing, material synthesis techniques, and molecular dynamics, a solid foundation has been laid for the in-depth study of hydrated calcium silicate.

Studying the crystal structures of tobermorite or jennite are the two commonly used methods of establishing the hydrated calcium silicate model; the amorphous hydrated calcium silicate and the crystal structures of tobermorite have similar characteristics and the same components, all of which are layered, with layers of silicon chains and layers of calcium atoms forming their main structure [16]. The layered structure containing single chains of silica-oxygen tetrahedra ($[\text{SiO}_4]^{4-}$) constitutes tobermorite and jennite, and the bridge tetrahedra plus two non-bridge tetrahedral units are repeatedly extended to form silica-oxygen tetrahedral chains. The sizes of tobermorite are classified as 9 Å, 11 Å, and 14 Å, depending on the size of the layer spacing, their calcium–silica ratios (C/S) range from 0.67 to 1.0, and the tobermorite crystal model established by Hamid is 11 Å (C/S = 1.0) [17]. The jennite crystal model has a C/S of 1.5, and its chemical component formula is $\text{Ca}_9\text{Si}_6\text{O}_{18}(\text{OH})_6 \cdot 8\text{H}_2\text{O}$ [18].

In addition to the Taylor model above, the main structural models are as follows: the solid solution model, the R–G model, the CM model, and the SLGS model. Many of these

models are very similar, but the adaptability of different model applications varies. The main characteristics of the different models are shown in Table 1.

Table 1. The main characteristics of different hydrated calcium silicate gel models.

Model Classification	Founder	Established Foundation	Structural Characteristics	Application Characteristics
Taylor	Taylor	Tobermorite, Jennite	Silica tetrahedron	Hydration, mechanical properties.
R-G	Richardson, Groves	Tobermorite, Jennite, $\text{Ca}(\text{OH})_2$	Silica tetrahedron [19]	Not sensitive to temperature.
CM	Jennings	Hydration component	Spherical element [20]	Shrinkage and creep.
Solid solution	Kantro	Thermodynamic theory	Sandwich construction [21]	Cement hydration.
SLGS	Setzer	Surface physical theory	Solid-liquid-gel system	Adverse static electricity, separation pressure.

3.2. Molecular Structure Model of Calcium Silicoaluminate Hydrate Gel

Calcium silicoaluminate hydrate gels are polymeric silicates (aluminates) that share some similarities with hydrated calcium silicate gels. The microstructure of calcium silicoaluminate hydrate ranges from disordered to ordered and from amorphous to semi-crystalline in a three-dimensional network structure. This is due to the low crystallinity and low long-range ordering of the gels, and therefore it is not easy to describe the microstructure. The detailed microstructure of calcium silicoaluminate hydrate gels is still under debate. There are two general views, namely, a tobermorite-like-structure and zeolite-like-structure model. In most studies, the analysis and processing of data are based on the microstructure of the tobermorite-like structure for studying calcium silicoaluminate hydrate gels.

Hou et al. studied the molecular structure (MS) of $\text{Ca}_3\text{O}_5\text{Si}$ -slag composites at different temperatures [22]. They applied MD methods to simulate the MS and MP of calcium silicoaluminate hydrate gels. Since the reaction force field (ReaxFF) is applied to the hydrogenation reaction of calcium silicoaluminate hydrate gel with different components, ReaxFF can optimize and reflect the interactions between different elements. The microstructure and properties of the materials at different temperatures were explored by modeling three calcium silicoaluminate hydrate gels.

Zhang et al. studied the influence of corrosion inhibitors on cement-slag composite slurry under the action of seawater erosion using MD simulation [23]. In this work, the atomic model consists of three units: the calcium silicoaluminate hydrate nanopore, the corrosion inhibitor molecule, and the sodium chloride solution simulating the transportation of erosive ions in the capillaries of the cementitious material and the effect on durability.

3.3. Molecular Structure Model of Sodium Aluminosilicate Hydrate Gel

The geopolymers consists mainly of sodium aluminosilicate hydrate gel, and has three different basic composition units. Sodium aluminosilicate hydrate gel has striking similarities to sodium alu-silicate glasses. The results of extensive spectroscopic studies revealed that both are three-dimensional network structures formed by interconnecting the ring chain structures of silicon and aluminum tetrahedra. The thermology and formation mechanism of geopolymers [24], structural evolution [25], durability [26], mechanical properties [27], fiber reinforcement [28], are the topics of many research studies on the engineering application of the above [29]. MD simulations are rapidly developing in the study of geopolymers through the continuous advancement of research tools. Bagheri et al. researched the influence of boron on sodium aluminosilicate hydrate gels by constructing a model of geopolymers [30]. Sadat et al. carried out a molecular dynamics study of polymers with silica glasses as a fundamental model, and analyzed the interplay between atomic composition, model structure, and MP [31]. Hang et al. investigated the influence of water molecules on the structure and MS of sodium aluminosilicate hydrate gels [32].

Chen et al. used MD simulations through a polymerization approach to building a sodium aluminosilicate hydrate gel model [33].

Hou et al. investigated the MS and dynamic properties of sodium aluminosilicate hydrate gels at high temperatures of 300–1500 K, using molecular dynamics [34]. It was shown that both Al-O-Si and Si-O-Si bonds in sodium aluminosilicate hydrate gels were disrupted with increasing temperature, and the MS of sodium aluminosilicate hydrate gels converted into a branching structure. In addition, as the temperature rises, the self-diffusion rate of molecules increases.

To investigate the effect of Ca^{2+} on the microstructure and MP of geosynthetics, Wang et al. developed a molecular model of geosynthetics using molecular dynamics modeling [35]. By setting a constant $\text{H}_2\text{O}/\text{Si}$ ratio and different ratios of Si, Al, and Ca atoms, they constructed a molecular model. Since the SiO_2 glass molecule was a $[\text{SiO}_4]$ tetrahedra, its MS was the same as the conclusions presented by Davidovits [36]. Hence, the initial structure of the geopolymers molecular model used the SiO_2 molecular construction. Molecular models with different ratios of Si, Al, and Ca atoms were built by randomly replacing Si atoms with Al atoms and adding appropriate amounts of Na^+ and Ca^{2+} ions, after the system was equilibrated. The results showed that the calcium ions in the geosynthetic model improved the stability of the molecular structure.

Simin et al. used the Walkley model to establish the sodium aluminosilicate hydrate gel model, whose structure was improved when the Si/Al ratio was 2 [37,38]. This silica-calcium ratio is used the most, and is widely used in geopolymers. Depending on the position of the atoms, a charge balance is applied and Si and Al atoms are used as the basic units of the model. In contrast, H_2O , Na^+ , and Al are dispersed in the structure. Since the structure of the sodium aluminosilicate hydrate gels is irrational, amorphous units were created as models to show this characteristic.

Gideon et al. investigated the fracture toughness of hydrated sodium aluminosilicate gels formed from alkali-activated fly ash [39]. The sodium aluminosilicate hydrate gel structure and its fracture were simulated using MD. A molecular model with an atomic spacing of 2 Å and containing Al, Na, Si, and O atoms was first constructed. Then an initial crack was set in the sodium aluminosilicate hydrate construction by removing the original crack region. A pre-existing defect with dimensions of 43 Å × 10 Å × 35.8 Å was added. The fracture properties were then studied by applying uniaxial tensile loading.

Mohammad et al. used MD simulations to forecast the elastic-plastic response of geosynthetic binder (GB) under the action of nanoindentation, and developed a molecular model [40]. Simulations were studied using different Si/Al ratios and the same Al/Na. After the system was equilibrated, the (fewer than four) surface atoms under ligand of Si and Al were saturated by the addition of -OH groups, and one H atom was added for each dangling O. The accuracy of the simulated structures was demonstrated by comparing the IR spectra of GB and pure silicon.

Chen et al. studied the microstructure of hydrated sodium alum inosilicate gels through MD simulations using ReaxFF force fields, and constructed a molecular model of sodium aluminosilicate hydrate gel using Si(OH)_4 and Al(OH)_3 polymerization [33]. It was found that the existence of pent-coordinated Al in the established sodium aluminosilicate hydrate gel model indicated that not all of the Al in the hydration products generated tetrahedral joint structures.

4. Overview of Supporting Experimental Techniques for MD

The characterization of hydrated calcium silicate gels, both the hardness and the elastic modulus, is essential for the research into MP. The measurement of the MP microstructures at the nanoscale relies on the extensive use of experimental techniques. The accuracy of molecular dynamics simulations is verified by experimental data, and the results of molecular dynamics simulations can further guide the experiments. X-ray diffraction (XRD) [41] nuclear magnetic resonance (NMR) [42], Fourier-transform infrared spectroscopy (FTIR) [43], synchrotron [44] and neutron scattering [45] have been widely used to

explore the crystal phase and chemical bond characteristics of cement-based materials [46]. Predecessors have studied the nucleation process of the gel in cement-based materials through advanced experimental techniques, characterized its microstructure [47,48], and explored its nanomechanical properties [49,50]. The application of commonly used experimental techniques in molecular dynamics studies is briefly described.

4.1. High-Pressure X-ray Diffraction Analysis (HP-XRD)

The HP-XRD technique can be used to determine the bulk elastic modulus of the hydrated calcium silicate gel/polymer and to study the effect of the polymer on the crystal structure MP of the gel. The Monteiro team has successfully measured the bulk elastic modulus of various cement-based materials such as tobermorite, C₃A, calcium aluminate hydrate and calcium aluminum carbonate using HP-XRD technology, and the experimental results are basically consistent with the simulation method. Geng et al. have conducted HP-XRD experiments on low-crystallinity calcium silicoaluminate hydrate gels. The results show that a more realistic elastic modulus can be obtained through Rietveld refinement analysis of the limited characteristic peaks existing in the gels, and it is found that a higher calcium–silicon ratio and aluminum–silicon ratio have different strengthening mechanisms for calcium silicoaluminate hydrate gels [51,52]. The XRD analysis results of the synthesized calcium silicate hydrate from Shi Lei [53] show that there are obvious diffraction peaks in the range of $2\theta = 2\text{--}10^\circ$, and it is inferred that the obtained calcium silicate hydrate has a layered structure.

4.2. Nanoindentation

Nanoindentation is widely used for quantitative testing of cement-based materials [54,55]. The nanomechanical properties of hydrated calcium silicate gel have significant influence on the macroscopic performance of cement-based materials. The results of the nanoindentation test on muddy water purification show that the hydrated calcium silicate gel can be divided into two different states, of low density and high density, and that the elastic modulus varies greatly [56]. Although it is difficult to distinguish pure hydrated calcium silicate gels from hydrated mixtures, some researchers have also performed nanoindentation tests on synthetic hydrated calcium silicate gels. The results show that the hardness and elastic moduli of the synthesized hydrated calcium silicate gel are the same as those of the actual hydrated product. The porosity of the material has a more significant effect on the experimental results than the calcium–silicon ratio [57]. In addition, Ulm et al. found that the creep characteristics of concrete can be effectively simulated on a macroscale, using nanoindentation technology. They concluded that the creep mainly comes from the relative sliding of hydrated calcium silicate gel particles at the nanoscale [56]. Jennings et al. [58] found through nanoindentation technology that the elastic modulus frequency of calcium silicate hydrate gels produced in the initial stage of hydration presented a unimodal distribution mode, and the elastic modulus frequency of calcium silicate hydrate gels changed into a bimodal distribution mode before the end of the hydration reaction, with the peak modulus being 19.7 ± 3 GPa and 27 ± 3 GPa, respectively.

4.3. Scanning Electron Microscope and Energy Spectrum Analysis (SEM-EDS)

A scanning electron microscope (SEM) scans the sample by electron beam, receives the secondary electrons released by the sample, and analyzes the surface or cross-section morphology of the sample. Energy spectrum analysis is used to detect the chemical composition of the sample, and its detection resolution can reach the micron-scale range, including point scanning, line scanning, surface scanning and other detection methods. Yang Jun [59] used SEM-EDS and ²⁹Si NMR to study the effects of SO₄²⁻ erosion on the composition and microstructure of calcium silicoaluminate hydrate gel in cement-slag slurry.

4.4. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TG) is a widely used method for the detection of gelled materials [60,61]. The basic chemical composition of the gelled material can be quantitatively characterized by thermogravimetric analysis, the basic principle of which is to determine the mass loss of the sample material when heated under specific conditions. The thermogravimetric analysis of hydrated calcium silicate gel shows that the loss of structural water and the decomposition of calcium hydroxide are the main causes of sample quality loss in different temperature ranges. Lucia et al. [62] used the thermogravimetric analysis (TGA) curve and the derivative thermogravimetric analysis (DTG) curve to analyze the thermal decomposition of cement slurry.

4.5. Fourier-Transform Infrared Spectroscopy (FTIR)

Fourier-transform infrared spectroscopy (FTIR) detects structures and chemical bonds in sample molecules. In cement chemistry, infrared can be used to detect chemical bonds in samples and to make a semi-quantitative analysis, according to the strength of the spectrum, to determine the relative content of the group change, so as to analyze the degree of polymerization of silica tetrahedron and aluminum oxide tetrahedron doping in calcium silicoaluminate hydrate gel. Factors affecting the spectral band include: molar mass, activation temperature, pH, activator concentration, Ca/Si ratio, Si/Al, etc. [63]. However, calcium silicate hydrate gel is a kind of poorly crystalline material, and its FT-IR test results have the same diffusing peak as XRD test results, so the analysis is more difficult. The vibration information of the four groups in the hydrated calcium silicate can be obtained by infrared analysis, which is important for the study of the degree of polymerization of silica tetrahedra in hydrated calcium silicate. Catherine A. et al. [64] used FTIR to study the structural change in polymer based on fly ash, and verified the relative change in the Si/Al ratio of the alkali-excited gel.

4.6. Nuclear Magnetic Resonance (NMR)

Nuclear magnetic resonance technology is mainly used to analyze the chemical environment of an element. The main elements in cement are ^1H , ^{17}O , ^{19}P , ^{23}Na , ^{25}Mg , ^{27}Al , ^{29}Si , ^{43}Ca , and so on. The phase and microstructure of gelled materials can be measured using NMR, and the corresponding NMR spectra can also be used for elemental analysis. The microstructure of the hydration products and the corresponding MP [9,65,66] were studied using nuclear magnetic resonance technology. Li B. [67] analyzed the properties of hydration products using XRD and an SEM and EDS spectrometer, ^{29}Si and ^{27}Al nuclear magnetic resonance, and other testing methods, and concluded that the introduction of polyaluminum chloride could reduce the average chain length and polymerization degree of calcium silicoaluminate hydrate gel molecules in hydrated slurry, and increase the proportion of Al-substituted silicon in calcium silicoaluminate hydrate gel. Ivan [68] used ^{29}Si nuclear magnetic resonance to study the structure of calcium silicate hydrate, and believed that changes in the ratio of calcium to silicon would affect the degree of polymerization of calcium silicate hydrate.

5. Study of Basic MP of Cement (Geopolymer)-Based Composites

The force field is a general term describing the interaction of potential fields between atoms. It is the core of molecular dynamics calculations, and affects the reliability of structural simulations. As the basis of molecular dynamics simulation, the force field is a function used to calculate molecular potential energy and atomic spacing. The molecular force field consists of three parts: the atomic type, the force field potential function and the parameters of the potential function [46]. For different models and different research contents, different force field parameters and different potential energy functions should be selected. For cement-based composite cementitious materials, the characterization of hardness and the modulus of elasticity are critical for the study of mechanical properties. The MS and MP of cementitious composite gels at the microscopic level were successfully

simulated by various force fields. See Table 2 for the characteristics of various common force fields of cement-based composites.

Table 2. Summary of common force field characteristics.

Force Field	Scope of Application	Force Field Function Composition	Category	Features
CVFF	Organic molecules	Coulomb force, Van der Waals force, total non-bonded energy.	Classic Force Field	Structure and binding energy of the computing system.
ClayFF	Structure, surface and interface of complexes and their solids/liquids.	Coulomb force, Van der Waals force, stretching potential energy, and distortion potential energy.	Traditional Force Field	Force field model based on single-point charge water molecule model.
ReaxFF	Silicon–water interfaces, gels, and nanocrystals.	Coulomb force, Van der Waals force.	Second-Generation Force Field	Describes the interactions of different elements.
COMPASS	Organic/inorganic small molecules, metal oxides.	Bonding energy, interaction energy, and non-bonding interaction energy.	Second-Generation Force Field	Thermodynamic properties.

5.1. Research on MP of Portland Cement-Based Composites

ClayFF, ReaxFF, and the COMPASS force fields are often used to model the structure of atoms of Portland cement-based materials.

Hou et al. studied the effect of variation in the Ca/Si ratio on the MP of composites using the ClayFF force field. Because of the MS and dynamic differences in the lamellar construction, the hydrated calcium silicate gel model exhibits the mechanical behavior of a non-homogeneous material [69]. The tensile strength and Young's modulus of the hydrated calcium silicate gel are similar to the results obtained from realistic experiments.

Hou et al. studied the reaction of bound water in hydrated calcium silicate gel nanopores [70]. They simulated hydrated calcium silicate gels using ReaxFF force fields and modeled them using calcium silicate skeletons in conjunction with Pellenq et al. The simulation outcomes show that the MP of hydrated calcium silicate gels is affected by the average chain length of calcium silicate, and the number of interlayer water molecules showed a positive relationship with the ratio of the Ca and Si atoms. The MP of the structure was tested using simulated uniaxial tensile tests. The tensile strength and Young's modulus in the X, Y, and Z directions showed a decreasing trend with the increase in ratio of the Ca and Si atoms. It has also been found that the MP of materials can be affected by nanopores [71].

Using a COMPASS force field, Murillo et al. developed an MD model based on the generation of hydrated calcium silicate perlite. Murillo et al. analytically studied the shear deformation and damage of hydrated calcium silicate gels, and the jennite variation under shear deformation [72]. Perlite exhibits a linear elastic property under shear deformation, and the shear stress and shear deformation result in an approximate agreement with the data from Pellen simulations, followed by yielding and plastic deformation.

Hou et al. used ReaxFF force fields for MD simulations, including model construction and mechanical testing [73]. The mechanism of action between graphene/graphene oxide and hydrated calcium silicate gel was studied. It was found that the combination of graphene oxide increases the flexural strength of cement-based materials. This is mainly because of the hydration reaction and the nano-filling effectiveness of the cement matrix. The high viscosity and plasticity enhancement of graphene oxide-reinforced cement composites are mainly due to hydrogen bonding and covalent ionic bonding. Combined with the macroscopic experimental results, MD simulations explain the difference in the reinforcement mechanisms of graphene oxide and graphene on cementitious materials. Zeng et al. added graphene oxide to hydrated calcium silicate to form cement composites, using MD simulation [74]. They found that the addition of graphene had a significant effect

on the Young's modulus of the hydrated calcium silicate gel. Also, the higher the amount of graphene oxide added, the greater the increase in the Young's modulus.

Lin et al. studied the spread of stress waves in hydrated calcium silicate loaded by planar impact compression in the direction of the water layer. They performed MD simulations using the ClayFF force field [75]. The particle velocities were adjusted to obtain stress waves of different intensities. The results show that the impact intensity causes the hydrated calcium silicate to be in variable elastic-plastic states. Different particle velocities produce continuous elastic waves, shock waves, and double-wave states.

Xu et al. investigated the microstructure of perthio-phosphogypsum slag cement (PPSC) using laboratory tests and MD simulations [76]. The study provided a basis for the multiscale regulation of its chemical composition design. To better investigate the influence of different molecular ratios on the mechanical properties of PPSC, MD simulations were used, based on the chemical composition molar ratios, to construct the initial model of PPSC structure using the amorphous cell module. The model was brought to equilibrium by three structural optimizations (the conjugate gradient method, the maximum rate of descent method, and Newton's method) at the COMPASS force field and at a 298 K temperature. After that, the effect of different molecular contents on the effect of alkali excitation and other mechanical properties was investigated.

Through the above study cases, the corresponding simulation conclusions can be obtained for different study objects, application software, and force fields, as shown in Table 3.

Table 3. Conclusions of the MS of MP of Portland cement-based materials.

Reference	Research Subjects	Force Field	Software	Main Conclusions	Comparison Experiments	Comparison of Results
Hou et al. [69]	MS of C-S-H	CLayFF	LAMMPS	Long silicate chains can improve strength and plasticity.	Tensile test, nanoindentation test.	Approach
Hou et al. [70]	Water/ion and Tobermorite interface.	ReaxFF	LAMMPS	Decrease in tensile strength and Young's modulus with increasing Ca/Si ratio.	NMR, QENS, PFGR, nanoindentation.	Matching
Hou et al. [73]	Graphene/Graphene Oxide.	ReaxFF	LAMMPS	Bonding and plasticity from hydrogen bond and covalent ionic bonding. C-S-H in elastic, elastoplastic or impact state at different impact strengths.	Compression and bending test.	Matching
Lin et al. [75]	Mechanical response under impact loading.	ClayFF	LAMMPS	elastoplastic or impact state at different impact strengths.		
Xu et al. [76]	Microstructure of perthiapatite gypsum slag cement.	COMPASS	Materials studio	SiO ₂ /Al ₂ O ₃ and CaO/SO ₃ molar ratios affect the strength and alkali excitation effect of PPSC.	Pressure resistance test, XRD.	Matching

5.2. Study of Mechanical Properties of Geopolymer-Based Composites

The ReaxFF force fields and COMPASS force fields are commonly applied to construct the atomic structure of sodium aluminosilicate hydrate gel gels. In ReaxFF, the bond order scheme uses parameters such as interatomic distances to construct chemical reactions. This parameter is continuously updated to construct the breaking and forming of chemical bonds. The COMPASS force field is the most widely used type of force field in covalent bond simulation systems.

Wang et al. investigated the effect of Ca²⁺ quantity on the MS and MP of geopolymers in the Na⁺ and Ca²⁺ coexistence system, using MD simulations [35]. Research results showed that the stability of the three-dimensional structure of geopolymers increased with increasing Ca²⁺ content, while other property indices were also found to increase with increasing calcium–aluminum ratio, such as elastic modulus, compressive strength, and density.

Hou studied the mechanical performance of sodium aluminosilicate hydrate gels at different temperatures, using uniaxial tensile tests. In the tensile tests, it was found that the

aluminosilicate network depolymerized into a branched structure, which greatly affected the tensile load [34]. At the same time, the fracture of the aluminosilicate backbone was accompanied by hydrolysis reactions, which deteriorated the structure further. The tensile strength and stiffness of sodium aluminosilicate hydrate gels were significantly weakened, due to the reduced chemical bond stability at high temperatures. However, the ductility of the sodium aluminosilicate hydrate gel was improved, due to a higher degree of structural arrangement in the yielding phase, partly due to a lower water intrusion rate.

Tian et al. used MD simulations to model static interfacial interactions between the main hydrated components of geopolymers and different crystalline surfaces of total minerals [77]. Simulations were performed at the microscopic level, based on the mode of action and intensity analysis. At the same time, they discussed the dynamic mechanical behavior of the different interfacial interactions from the nanoscale, using the uniaxial tensile method. The simulation results show that each crystalline surface of CaCO_3 exhibits stronger surface energy and surface infiltration than SiO_2 , and stronger interfacial interaction potential and tensile stress with sodium aluminosilicate hydrate and calcium silicoaluminate hydrate. However, the anisotropy of the CaCO_3 crystalline surface is obvious, and the performance is less stable than that of SiO_2 . The interaction potential between the geopolymer and the aggregate mineral is mainly provided by the electrostatic potential. This is due to the fact that the electrostatic interaction of the mineral interface and the interaction zone is characterized by water molecule aggregation and obvious hydrogen bonding. At the same time, water molecules are coordinated with Ca^{2+} and Na^+ to form hydrated ions, which helps ions to migrate and precipitate, and helps nucleation growth on the mineral surface. In the uniaxial tensile simulation, the tensile failure mechanism at the interface of the geopolymer and aggregate minerals includes two stages: the first stage ($0 \text{ nm} < \text{interface displacement } d < 0.15 \text{ nm}$) mainly overcomes the electrostatic effect of interfacial interaction; the second stage ($0.15 \text{ nm} \leq d \leq 0.3 \text{ nm}$) mainly overcomes the hydrogen bonding effect.

Mohammad et al. investigated some properties of amorphous geopolymer binders (GBs) under spherical nanoindentation, using MD simulations [40]. These include the mechanical response, the SiAl ratio of the GB, the indenter radius, and the rate of loading. The evolution of the Al-O and Si-O bonds indicates a corresponding increase in the number of broken bonds as the indenter radius decreases. It is also found that the evolution of the bond angles correlates with the stress in the GB structure.

Gideon et al. investigated the fracture toughness of sodium aluminosilicate hydrate gels which were generated from alkali-activated fly ash [39]. The fracture toughness of sodium aluminosilicate hydrate was discovered to be well correlated with the results of nanoindentation experiments through MD simulation studies using the ReaxFF force field. It is shown that the combination of nanoindentation experiments and MD simulations can optimize the design of sodium aluminosilicate hydrate materials to improve the material properties.

Through the above research cases, corresponding simulation conclusions can be obtained for different research objects, the application of software, and force fields in the study of mechanical properties of geopolymer matrix composites, as shown in Table 4.

Table 4. Conclusion of MD of MP of geopolymer.

Reference	Research Subjects	Force Field	Software	Main Conclusions	Comparison Experiments	Comparison of Results
Hou et al. [40]	Mechanical properties of NASH at different temperatures.	ReaxFF	LAMMPS	As the temperature increases, the tensile strength and stiffness of N-A-S-H gel decreases, but the ductility increases.	NMR,	Hou et al. [40]

Table 4. *Cont.*

Reference	Research Subjects	Force Field	Software	Main Conclusions	Comparison Experiments	Comparison of Results
Wang et al. [41]	Effect of calcium content on NASH.	Compass	Materials Studio	The modulus of elasticity, the compressive strength and density all increase monotonically with increasing calcium content.	Modulus of elasticity, compressive strength.	consistent
Mohammad et al. [57]	Amorphous geopolymers.		LAMMPS	The hardness increases as the indenter size decreases.	NMR, IR, spectra, X-ray.	matching
Tian et al. [77]	Static interfacial interactions of different crystal surfaces.	Compass	Materials Studio	Compared with SiO_2 , the interfacial interaction potential and tensile stress of each crystalline surface of CaCO_3 with geopolymers are stronger. The interface strength can be improved by adding a graphene layer or using modified epoxy resin.	Uniaxial tensile test.	approximate
Ashraf A.Bahraq et al. [78]	Adhesion properties of cement/epoxy interface	Compass	Materials Studio	Link the thermal energy storage parameters of the atomistic main phases of OPC-based paste and geopolymer with the homogenized upper meso-/macroscale values.	Differential scanning calorimetry, thermal conductivity.	
Antonio Caggiano et al. [79]	thermal properties in ordinary Portland cement and geopolymer pastes.	ReaxFF.				More reasonable

6. Investigation of MP of Cementitious Composite/Reinforcements Interface

6.1. Investigation of MP of Steel/Cementitious Material Interface

Concrete has become the most used construction material, with its low cost, easy construction, and high durability, but it also has significant defects in terms of low tensile strength and easy cracking. Therefore, the preparation of reinforced concrete by configuring steel bars in concrete can enhance the tensile strength of plain silicate concrete. But, during the service of reinforced concrete, the structural damage caused by cyclic loading seriously affects the construction. During the service of reinforced concrete, the reinforcement passivation film contributes an active effect in improving the durability and erosion resistance. However, after decades of research, there is no consistent conclusion on the atomic structure of this passive film.

Xu et al. studied steel passivation films through molecular dynamics studies [80]. They found that the various types of atoms of Fe and $\gamma\text{-Fe}_2\text{O}_3$ rely on chemical bonds such as metallic and ionic bonds, respectively, while the interlayer structure of $\gamma\text{-FeOOH}$ relies on intermolecular forces. This leads to weaker forces in the interlayer direction of $\gamma\text{-FeOOH}$, which is more prone to damage; when uniaxial loading is applied to the model, it can be seen from the schematic diagram of the distribution of allotment numbers that the coordination number of Fe changes randomly in the model, and although no obvious damage occurs in the middle of the $\gamma\text{-Fe}_2\text{O}_3$ model initially, it still shows obvious randomness at the later stage of the simulation. The analysis of the coordination changes shows that the Fe structure and the $\gamma\text{-Fe}_2\text{O}_3$ structure show isotropy, while the $\gamma\text{-FeOOH}$ shows anisotropy; the integrated stress-strain curve shows that, for the three types of components of the steel passivation film, Fe has the best mechanical properties, followed by $\gamma\text{-Fe}_2\text{O}_3$, and the worst is $\gamma\text{-FeOOH}$. Therefore, in the actual tensile process, the damage of the steel passivation film under tensile load occurs from outside and inside.

6.2. Investigation of MP of Synthetic Fiber/Cementitious Material Interface

In addition to the use of steel, the adding of fibers to enhance the MP has also been used extensively [81]. Among them, the widespread use of synthetic fibers results from their

advantages, such as low cost and high durability. Wang et al. conducted an MD simulation investigation on the shear strength of CSH compared with polymer fibers [82]. To reveal the mechanism of the difference in shear strength at the interface between different polymer fibers and cementitious materials, they analyzed the molecular structures and dynamic properties of polyphenylene acid (PAA), PA, and polyvinyl alcohol (PVA). The hydrated calcium silicate model was simulated, based on tobermorite crystals [83]. Tobermorite crystals are widely used to model the MP of hydrated calcium silicate [71].

Cellulose chains composed of duplicated units are commonly applied to build molecular models of amorphous cellulose (AC) [84]. In a study by Liu et al., cellulose composed of I β and AC was used to analyze binding energy and the influence of each one on the other between the cellulose-hydrated calcium silicate interface, using MD simulations [85]. However, due to their complex chemical structures, tobermorite and ionomer are often used in MD simulations [86]. Liqueur et al. discovered that the silica chains of hydrated calcium silicate are shorter than that of tobermorite [87]. Allen et al. discovered the molecular formula of hydrated calcium silicate [88]. To enhance the accuracy of the molecular structure simulation of hydrated calcium silicate, Qomi et al. removed silicon dioxide from the tobermorite model to form hydroxyl groups (-OH), thus constructing a faithful hydrated calcium silicate model [89].

Facundo et al. found that the tensile strength of the fibers is affected by the inclination, through pull-out tests [90]. MD simulations on the microscopic level can corroborate the analysis of the macroscopic experimental results [91]. Oral et al. discovered that the adhesion strength between composite interfaces can be affected by water molecules [92]. Hou et al. found that the interfacial adhesion strength between hydrated calcium silicate and polymers was influenced by the polarity of the functional groups [93]. It was shown that polymers with different functional groups, such as polyaniline and polyethylene glycol, all modify the microstructure of hydrated calcium silicate gels to some extent, and can improve the properties of the composites [94]. Previous studies on clay-polymer systems have shown that molecular dynamics can successfully characterize the connectivity and interaction mechanisms at the clay-polymer interface [95]. Meanwhile, more sophisticated and accurate interfacial force fields have been developed [96,97]. Hydrated calcium silicate gels and clays have the same interlayer structure, and therefore can be used as a reference for each other.

Zhou demonstrated through molecular simulations that the intercalation of polymers (PAA, PVA, PEG) all significantly improved the extensibility of hydrated calcium silicate gels in the process of stretching [98]. The interlayer polymers could effectively hinder the rapid tensile damage in the weak region of the matrix, and the polymer macromolecules fractured into small molecules under stress, which then filled the hydrated calcium silicate gels, delaying the fracture failure of the composite. The XRD and $^{29}\text{SiNMR}$ tests showed that the incorporation of PAA and PVA disturbed the orderly accumulation of calcium-silica layers in the hydrated calcium silicate gels. It can be speculated that they are attracted to the surface of the hydrated calcium silicate gels or to the defects between the layers. Based on HP-XRD, molecular dynamics, nanoindentation, NMR, and other test and simulation methods, it can be inferred that the intercalation probability of PEG molecules is low, and may exist in the pores between the hydrated calcium silicate gel, thus reducing the stacking density and indentation modulus of hydrated calcium silicate particles. However, there is still some interaction between PEG and hydrated calcium silicate gel particles, which keeps the creep modulus of the matrix at a high level.

Wang et al. also found that fiber type and H-bonding have a significant effect on interfacial strength [81]. By studying the loss of energy, they found that the interfacial strength was greatest for PAA, followed by PVA, and least for PP. Through chemical bond stability studies, they found that the bond energies of the three fibers, PAA, PVA, and PP, showed a sequential decrease. The researchers studied the MP of hydrated calcium silicate mainly by comparing it with the results of nanoindentation experiments, but also, of course,

by comparing it with the results of other experiments (SANS, NMR, etc.), which makes the experimental data of molecular dynamics reliable.

Ohno and Li investigated the interfacial nature of strength-optimized PVA fibers in a fly ash-based polymer matrix [99]. They found that the chemical binding energy (G_d) values were almost five times higher compared to conventional SHCC materials, while the tendency for friction bonding was much lower. Hang et al. found that the G_d was mainly related to the microstructure and chemical properties [100]. Nematollahi et al. found that the fiber bridging strength of the composites was strongly correlated with the strong chemical bonding of the PVA fibers [101].

Zhang et al. investigated the adhesion mechanism, interfacial nanostructure, and associated cohesive performance of PVA fibers with sodium aluminosilicate hydrate gels and calcium silicoaluminate hydrate gels in an alkali-activated slag/fly ash (AASF) matrix [102]. This study used a combination of MD simulations and experiments. MD simulations showed that the elemental content ratio had an important effect on the bonding performance.

6.3. Investigation of MP of Synthetic of Plant Fiber/Cementitious Material Interface

Plant fibers can enhance the physical properties and reliability of cementitious materials. However, cellulose fibers have different structures. It is important to study the interaction and reinforcement principles of cellulose fibers with cementitious materials at the microscopic level. Natural cellulose fibers have three chemical structures, namely, crystalline I α , crystalline I β , and the amorphous state. Investigators have modeled the molecular structure of I β and amorphous cellulose(AC) using MD simulation methods, and I β cellulose has better stability [103]. The main hydration product of normal silicate cement is hydrated calcium silicate [104]. Therefore, it is important to study the bonding theory of cellulose fibers with hydrated calcium silicate at the microscopic level.

Liu et al. [85] investigated the interaction mechanism of cellulose fibers with hydrated calcium silicate and its interfacial nanostructures, using MD simulations. Also, they constructed structural models of cellulose fibers and hydrated calcium silicate, based on the experimental results, and investigated the interface bonding properties and microstructure [105]. The results showed that the deformation of cellulose was limited during the hydration process. Wang et al. [106] evaluated the interfacial strength between carbon fibers and Ag nanoparticles using multiscale modeling and MD simulation.

Liu et al. studied the interfacial nature of nano-SiO₂ and jute fibers using a sol-gel method [107]. Due to the excellent surface properties of nano-SiO₂, its reaction with the hydroxyl groups on jute fibers should form a steady interface. Through macroscopic evaluation and MD simulations, it was found that the deposition effect of nano-SiO₂ affects the wettability of jute fibers and improves the surface energy and tensile strength of jute fibers, while the protective layer formed by nano-SiO₂ eliminates the stress concentration sites on jute fibers. It has also been found that C-O-Si chemical bonding enhances the interfacial bonding within this composite interface [108].

6.4. Investigation of the MD of Fiber-Reinforced Composite/Cement Matrix Material Interface

Fiber-reinforced composite (FRP) plates are widely used in the reinforcement of concrete construction because of their outstanding properties such as strength, durability, processing performance, strengthening ability, etc. The FRP plate-reinforced concrete structure works by load transfer through the joint surface of the two materials, with them thus bearing the load together. The in-depth study of this structure revealed that the interfacial bonding performance is the key to improving the reinforcement effect. Meanwhile, temperature, freeze-thaw cycles, cyclic loading, humidity, and chemical environment are also important factors affecting the bonding performance of the structure.

For carbon fiber FRP/concrete structures, Jiang et al. studied the influence of sulfate on their interfacial bonding nature, using the MD simulation method [109]. It was found that the adhesion at the interface of this composite structure was offered by ionic and hydrogen bonds. The physical and energetic barriers provided by the sulfate solution interfered

with the hydrogen bonds. The MD simulation method illustrates the microscopic adhesion mechanism at the interface of this composite, and analyzes the adverse effect of the chemical environment on the interfacial bonding performance from the microscopic aspect.

6.5. Study of the Mechanical Properties of Nano Interfaces

Nanomaterials have good reactive and ductile properties and are rich in exceptional fracture, mechanical strength, and impact toughness. By adding various types of nanomaterials, the toughness and other properties of concrete can be improved. To fully understand the properties of nanoconcrete, the interfacial properties between the cement hydrate and nanoparticles are required. Sanchez et al. studied the interfacial structure and kinetic properties between torbemorillonite and graphene oxide structures using MD simulations based on two different force fields, CVFF and ClayFF [110,111]. The comparison of graphene and graphene oxide revealed the introduction of hydrogen bonding networks and Ca^{2+} dielectric interactions on functionalized surfaces. The main factor in the interfacial interactions is the electrostatic force. Meanwhile, Alphabet et al. found that the electrostatic force of the functional group and its Van der Waals function are the determinants of the strength of the hydrated calcium silicate interface under the influence of graphene oxide [112]. Although the strengthening mechanism was not analyzed, it significantly improved its compressive and bending strength.

Researchers investigated the effect of graphene on hydrated calcium silicate. They found that graphene could improve many MDs of the hydrated products [113–115]. The novel hydrated calcium silicate nanomaterial carbon nanotubes (CNTs) are perfect structures, composed of one-dimensional carbon atoms. Hu et al. found that the compressive properties of carbon nanotubes were lower than the tensile properties at the nanoscale, through molecular dynamics studies [116]. Sindu et al. investigated the compatibility of five surfactants with hydrated calcium silicate and their dispersion in carbon nanotubes, and further demonstrated that the composite of carbon nanotubes with hydrated calcium silicate could significantly improve the material toughness [117].

7. Research Gaps in Critical Fields of MD for Cementitious Composites

Although molecular dynamics simulation is playing an increasingly important role in materials science research, it still lags behind other material fields such as metal materials, polymer materials, carbon nanotubes, and so on. The composition of concrete determines the diversity of its hydration products, and the external conditions of concrete determine the complexity of its interfacial chemical environment. At the same time, due to the different hydration (excitation) conditions of cement (geopolymer)-based materials, their structures and properties also show diversified characteristics. Although the current research on the cementing material has achieved certain results, there are still many problems to be solved:

The design of cement-based materials in current engineering practice is mostly based on macroscale considerations, and relies on traditional semi-empirical models, so the material characteristics at the microscale and nanoscale cannot be fully explored. It is still necessary to obtain more abundant experimental data through experimental means to support relevant simulation studies. For example, the nanoindentation test obtained the anisotropic mechanical properties of calcium silicoaluminate hydrate gel, and the test results were easily affected by the particle packing density of calcium silicoaluminate hydrate gel; therefore, more advanced technologies were needed to directly test the molecular mechanical properties of calcium silicoaluminate hydrate gel at various scales after its microstructural evolution, so that the simulated values could be compared and verified.

Most researchers use a single ideal model for analysis, but the coupling effects of different products, different ions, and different temperatures are not considered, and the time- and space-scales of molecular dynamics simulation are still limited to a very small range. For example, the change in the structural characteristics of hydrated calcium silicate gel under different calcium–silicon ratios and the influence of reaction time on the pore structure of calcium silicate hydrate, and the effects of temperature and humidity on the

structure of hydrated calcium silicate were studied by ^{29}Si NMR. Due to the time limit of the simulation, the loading rate of the tensile is many orders of magnitude higher than the actual tensile loading rate, which leads to the tensile strength measured by simulation far exceeding the actual value, and the actual tensile strength of the materials cannot be evaluated by simulation alone.

At present, the molecular dynamics simulation of calcium silicate hydrate is in the initial stage, and the establishment of the model and the study of structure and properties are mostly based on the comparison with the experimental results, and there is no recognized calcium silicate hydrate model. The selection of the force field and cell size in molecular dynamics simulations is still in the stage of experimental exploration.

8. Conclusions and Outlook

At present, the application of molecular dynamics to the study of cement (geopolymer)-based materials has achieved preliminary research results. This method has guiding significance for the study of the microcosmic principle of cement (geopolymer)-based material properties and the precise design of high-performance concrete. The application of MD to the design of nanoscale cement (geopolymer)-based materials is beneficial for improving the performance of cement (geopolymer)-based materials in engineering applications. In addition, the collaborative study of MD simulation and the macro performance test will greatly promote the research and engineering application of cement (geopolymer)-based materials.

Through the performance analysis of macroscopic experimental results and microscopic models of cement-based materials, it is found that molecular dynamics has a very important significance for the study of cement-based materials. Molecular dynamics simulation can quickly and easily analyze the mechanical properties, transport properties and interface properties of composite materials, and help to better explain the macroscopic properties of materials.

Molecular dynamics simulation can analyze deeply the specific action mechanism of two phases on the nanoscale, and can also be combined with experimental means to develop new composite materials.

Molecular-scale simulation research is mainly based on the hierarchical structure model. The mechanical properties of layered calcium silicate hydrate, calcium aluminosilicate hydrate and sodium aluminum silicate hydrate gel show anisotropy, and their molecular configurations are not unique. Existing structural models are fairly controversial. Therefore, it is necessary to build a more accurate defect-containing model to simulate the real structure and environment. In addition, the hydration products of cement (geopolymer) will also change with the changes in the surrounding environment and time, and with other factors. The effect of these factors on the properties of the material remains to be further studied.

There are few molecular simulated force fields applicable to cement (geopolymer)-based materials which are transplanted from other force fields, and the application range and characterization ability of different force fields are very different. The parameters such as atomic type and charge in the force field should be further optimized according to the chemical environment of cement-based materials, and the parameters should be adjusted by comparing them with the macroscopic experimental values, to improve the calculation accuracy of the force field.

It is necessary for further study, through a large number of experiments and MD simulations, to reveal in depth the internal mechanism of improving concrete performance, and to lay a theoretical foundation for preparing the next generation of (super) high-performance concrete.

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