Roadmap across the mesoscale for durable and sustainable cement paste – a bioinspired approach

Steven D. Palkovic¹, Dieter B. Brommer², Kunal Kupwade-Patil¹, Admir Masic¹, Markus J. Buehler¹, Oral Büyükoztürk^{1*}

¹ Department of Civil and Environmental Engineering, Massachusetts Institute of Technology, 77 Mass. Ave, Cambridge, MA, 02139, USA;

² Department of Mechanical Engineering, Massachusetts Institute of Technology, 77 Mass. Ave, Cambridge, MA, 02139, USA

To be submitted to: *Construction and Building Materials (CBM)*

Keywords: Cement paste, Durability, Sustainability, Multiscale, Mesoscale, Natural materials, Bioinspired

Abstract (max of 100 words)

In recent years, continuum and atomistic modeling of cementitious materials has provided significant advances towards studying the durability of civil infrastructure. An important frontier to understanding structure-property relationships is the “mesoscale”, which represents the bridge between underlying (e.g. molecular) processes and bulk macroscale behavior. This review highlights examples of a mesoscale approach within biological materials and emphasizes their applicability to the study and design of sustainable cement-based materials at multiple length scales. We propose a methodology focused on the coupling of computation and experiment for furthering our understanding of the microstructural properties that control the durability of hardened cement paste.

1. Introduction

1.1 Motivation: Design of Sustainable and Durable Cement Paste

Cement-based composites are one of the earliest examples of an engineered structural material. The Roman's developed lime-pozzolana cements which were used to construct buildings that exhibit exceptional durability and have survived for more than 2,000 years [1, 2]. Modern cementitious materials are based on Portland cement, a mixture of limestone and clay that is heated and ground to produce a multiphase clinker that was first used in the early 19th century. Both Roman and Portland cement-based materials were initially engineered through gradual empirical improvements due to the material's complexity and sensitivity to composition and environment. Recent developments in nanotechnology have allowed for significant advances from these primitive manufacturing methods by enabling the investigation of these materials at multiple length and temporal scales [3]. The growth of nanotechnology has also facilitated studies on how nature designs and fabricates advanced functional materials such as bone, nacre and deep sea sponge. These biological materials employ hierarchical structures to achieve remarkable material performance that is adapted to their distinct utilization within an organism. Material scientists have begun to replicate these systems to produce synthetic composites which mimic designs found in nature, however, these concepts have not been widely applied to cementitious materials. Therefore, the motivation for this paper is to develop a framework that combines modern characterization techniques with natural design strategies to improve and engineer the durability of cement paste for specific applications.

Cement paste is a model system for exploration because of its ubiquity in the built environment and adaptability to a wide range of mix compositions. This adaptability provides an opportunity to improve and tailor cement paste using locally available additives, deemed supplementary cementitious materials [4, 5]. The availability of local additives to a region

depends not only on natural resources, but also on its industrial landscape including energy and manufacturing infrastructure. The use of additives for clinker substitution has also been identified as a low cost and high-impact method of reducing the carbon footprint of a rapidly expanding global concrete industry [6]. Therefore, deriving functioning mixes tailored to local economies is both environmentally and economically sustainable. In many cases these additive candidates, such as fly ash or volcanic ash, are waste products which would otherwise require disposal. Phair presents a tutorial for evaluating and producing sustainable cement, and we refer the reader to this review for the general strategy [7].

In addition to the economic and environmental incentives, additives can be incorporated to produce materials with superior properties compared to Ordinary Portland cement (OPC) pastes. When additives with fine particle sizes are used they act as filler material which provides nucleation sites for additional hydration products, in addition to forming secondary hydration products if the additive is reactive in the alkaline pore solution. These materials have been shown to provide denser microstructures, stronger interfacial bonding and a corresponding higher compressive strength and stiffness than OPC pastes [8-10]. Furthermore, cement paste with additives have exhibited reduced permeability and diffusivity as a result of a more tortuous network of capillary pores which leads to a more chemically resistant composite [11-13]. Other studies have shown that incorporation of additives can also lead to a reduction in creep compared to OPC paste [14, 15]. These improvements in durability for construction building materials reduce the need for rehabilitation and maintenance, and promote longer lasting structures.

However, not all materials are viable additives, and in many cases the additives must be carefully proportioned and controlled to obtain a suitable building material. Effective material design requires an understanding of the role of additives and the origin of material behavior

within the resulting composite. Although there is a great deal of understanding for OPC pastes, a departure in composition towards supplementary cementitious materials leads to changes in structure which are not as well understood. There is now an opportunity to utilize these tools to formulate a general framework for characterizing cementitious materials that would enable additive selection to design durable and sustainable cement paste, which is the main concern of this review.

1.2 Problem Statement

The purpose of this paper is to review the existing knowledge concerning the characterization of cement paste and devise a framework to describe structure-property relationships of the material across orders of magnitude in length and time scales. To do this, we incorporate a multiscale approach combining experiments and computation to develop mesoscale models for connecting underlying structures and processes with bulk behavior. This framework is motivated by prior success investigating biological systems. Whereas biological materials use evolutionary pressures to design materials for specific applications, cement paste is a man-made example of how we try to utilize a variety of natural resources to engineer materials with desired properties. We propose that the construction and building material community can benefit by examining the design strategies of natural materials that enable exceptional material properties through hierarchical structures. Similarly, for cement-based materials one must elucidate the relevant length scale and microstructural features controlling durability of a proposed cementitious mixture. The complex nature of cementitious gel formation during hydration along with the variability in the resulting pore network of a hardened cement paste requires experiments to directly inform models. By understanding what mechanisms improve material

performance and how they originate during the fabrication of cement paste we can understand how to make more durable materials in the presence of a broad range of emerging additives.

1.3 Defining the Mesoscale for Cement Paste

The mesoscale is an open concept that is ambiguously defined because it is dependent on the specific material system and property being investigated [16]. Fundamentally, the mesoscale allows for the connection between lower length scale structures or processes and macroscale behavior. A mesoscale model should furthermore include the essential features necessary to study the origin of the macroscale material property being explored, and be relatively insensitive to underlying characteristics that are not considered. The material properties most relevant to cement paste are those controlling its durability, including elasticity, strength, fracture resistance, creep, shrinkage, setting (or hydration), aging, and resistance to chemical attack. These properties originate at varying length and time scales in the material's structural makeup, which prevents a single mesoscale model size or approach from being specified, and requiring a multiscale framework. More specifically, we hypothesize that the material properties cannot be tied to a single structural feature or length scale, and rather, require a concurrent consideration of the material hierarchy [17, 18].

Figure 1 provides an abstraction of cement paste at disparate length scales and illustrates the necessity of multiscale techniques. Cement paste contains many products that form during the reaction of water with Portland cement, but the principal hydrated phase is Calcium-Silicate-Hydrate (C-S-H) which forms about 60% of the material's volume [15, 19]. C-S-H is produced in conjunction with calcium hydroxide during the chemo-mechanical reaction with silicate phases (β -C₂S and C₃S) [20]. At the atomistic scale, a building block can be identified for the C-S-H phase, with adjacent calcium-silicate layers separated by an interface containing confined

water and held together by strong ionic-covalent bonds [21]. This building block is essential to the behavior of the overall system and controls the reaction and hydration of the material. At larger length scales, these building blocks assemble to form a disordered porous material [22, 23]. The local environment controls the kinetics of hydration and resulting packing efficiency of these building blocks as the material sets to form a rigid solid [24, 25]. At this scale, the presence of water within the hierarchical pore network has a significant impact on the shrinkage and creep behavior of the system [26, 27]. The size, shape, distribution, and connectivity of this pore network governs the permeability and diffusivity that controls the resistance to chemical attack and degradation. At larger scales, the binding phase forms a continuous matrix containing randomly distributed pores, secondary reaction products, unhydrated materials, and associated interfaces between phases. Macroscale mechanical properties such as elastic constants, ultimate strength and fracture resistance are controlled by the overall composite response at this length scale.

Fig. 1: A multiscale perspective for cement paste materials. **(A)** Building blocks describe the fundamental atomic interactions of the binder phase. **(B)** At larger scales, the binder

phase is composed of an assembly of building blocks that form larger structures resulting in a hierarchical pore network. (C) The binder phase is intermixed with pores, mineral and unhydrated phases to form a cement paste composite at the micron scale.

The appropriate mesoscale models for studying the origin of macroscale durability properties are identified in **Table I**. Stiffness, strength and fracture can be assessed through quasi-static studies, whereas shrinkage, creep, setting, aging, and chemical attack are dynamic phenomena requiring the consideration of long-term behavior. Within this review, methods for establishing and utilizing mesoscale models incorporating the key features identified at each length scale are discussed. Future pursuits of mesoscale modeling will further our understanding of structure-property relationships within cement-based materials. This knowledge will allow us to select and proportion local additives for the tailored design of innovative and sustainable construction materials.

Table I: Mesoscale connections between key features of a material microstructure and durability of cement paste.

Length Scale	Description	Key Features	Durability Properties
Building block (~ 1 nm)	Quasi-layered nanoscale structure of hydrated gels	Ionic-covalent bonds and interlayer water interfaces	Unit processes, chemical reactions
Building block assembly (~ 10-100 nm)	Building blocks arrange to form particulates of various size and shape.	Gel and capillary pores, charged pore solution, particle packing and density	Shrinkage, creep, setting and aging, chemical attack
Cement paste composite (~ 100 μ m)	Continuous hydrated matrix with randomly dispersed inclusions (voids, unreacted materials, secondary products)	Volume fraction, position, and morphology of phases, interfaces, pore network, microcracks	Elastic stiffness, ultimate strength, fracture toughness

1.3 Outline of the Review

In Section 2 we introduce the discipline of multiscale design through an exposition of strategies that have been proven in natural systems. Furthermore, we use examples of nano- and microstructural features in biological systems, which lead to exceptional durability, and provide comparisons to known mechanisms within cementitious materials. Section 3 provides a review

of the current understanding of cement paste structure and chemistry in the context of experimental and simulation-based investigations at multiple length scales. Our focus is on the use of experiments to develop robust computational models. We detail prior mesoscale studies on cementitious materials and outline general strategies for bridging both length and time scales with simulations in Section 4. A robust multiscale framework for the study and design of more sustainable cement-based materials is introduced in Section 5. In Section 6, we conclude and present our analysis in a broader context.

2. Nature as a Source of Inspiration for Durable Building Materials

Natural materials are widely studied because of their ability to achieve a combination of high strength and fracture toughness using a limited amount of available resources [28]. This behavior is fundamental for natural materials because they utilize simple building blocks, which arrange into hierarchies that often outperform properties of the building blocks themselves. These building blocks are composed of the 20 or so amino acids that, once encoded into proteins, fold and stack into secondary structures including α -helices, β -sheets or triple-helix of tropocollagen. These protein polypeptide chain motifs further organize at a supramolecular level (10-100 nm) to form protofilaments, microfibrils or nanocomposites which are often characterized by amorphous and crystalline domains [29]. At the micron level, these structures arrange to form fibers, the basic structural unit of many macroscopic biological materials.

Rubber-like protein materials such as elastin exhibit a combination of high resilience, large ductility and low stiffness which allow them to store significant amounts of elastic strain energy [30, 31]. In comparison, collagen fibers provide incredible energy dissipation and resistance to fracture (i.e. toughness), but are not nearly as deformable [32]. Mussel byssus threads and spider dragline silks are remarkably stiff, stretchy and tough, allowing mussels to

survive crashing waves and spiders to build superb aerial traps [33, 34]. The native silk fiber can be described as a semi-crystalline material within which macromolecular chains are oriented parallel to the fiber axis. It is widely accepted that highly ordered, crystalline regions play a major role in determining the strength and stiffness of silks, while the non-crystalline regions contribute to the elasticity of the material [35, 36]. In the case of mussel threads, the presence and specific organization of metal ions such as Fe(III) and Zn(II) play fundamental role in providing both high hardness and incredible fiber extensibility [37]. These examples of protein-based biological materials highlight how the control of molecular and nanoscopic building blocks can lead to remarkable variability in the macroscopic performance based on the needs of an organism.

A common design strategy in nature is the formation of a nanocomposite combining biopolymers with mineral nanoparticles (apatite, calcite etc.) to produce a composite material that is much harder and stiffer than the biopolymer while still being tougher and less brittle than the mineral alone [38]. **Figure 2** presents a comparison of the multiscale structures in cement paste with the hierarchical structures of bone, deep sea sponge, and nacre. We choose bone, nacre and sponge because they are nanocomposites which have been widely studied in the literature and share several similarities with cement paste. Bone is a composite of mineral and polymer phases [39-41]. The fundamental building blocks are collagen and carbonated hydroxyapatite, which aggregate into mineralized fibrils and then form into fibers and other higher-order structures. The high strength and toughness of bone is largely attributed to its flaw tolerance at the nanoscale [42] in combination with microcracking, crack deflection along interfaces, and fiber bridging at the micrometer scale [43, 44]. Analogously, nacre has a brick-and-mortar arrangement consisting of approximately 95% inorganic mineral tablets (in this case

208 carbonate-based aragonite) and 5% organic protein interfaces [45-51]. The durability of nacre
209 may largely be attributed to the strong interfacial bond and local asperities at the organic-
210 inorganic interface [51, 52], whereas larger scale mechanisms include the microscopic roughness
211 of brick layers that leads to toughening through shear-compression interlock [53]. Like nacre,
212 the structural hierarchies of the deep sea sponge spicule are a multiscale design which achieves
213 mechanical properties that go far beyond the relatively weak constituent materials. The
214 microscale consists of a composite containing cylindrical amorphous silica rods with remarkable
215 toughness, especially if compared to its industrial counterparts. The “onion”-like structure
216 characterized by intersilica layers that contain small amounts of proteins (silicateins) provides
217 crack arrest mechanisms and enables a flexural strength that is up to four times that of monolithic
218 synthetic silica [54, 55]. Unlike the order exhibited by the biological systems just described,
219 cement paste can be generally described as a random heterogeneous composite containing a
220 hierarchical distribution of pores. At the lowest length scales, the binding C-S-H gel phase is a
221 nanostructured material whose layered building blocks arrange to form larger nanoparticles,
222 whereas the microstructure is a composite of amorphous and crystalline phases.

Fig. 2: A comparison of the structural hierarchies existing in natural materials and cement paste, demonstrating the steps by which smaller pieces assemble to form larger structures. Images were adapted with permission from [38, 56-61]. Image of Silicatein Copyright 2007 National Academy of Sciences, USA. The atomistic C-S-H Structure Copyright 2012 American Chemical Society. The Photo of Killian Court was obtained under a Creative Commons Attribution-Noncommercial license. Microscopy images courtesy of Dr. James Weaver.

Despite differences in composition and structure for natural materials and cement paste, biological strategies to build materials can be a powerful source of inspiration for the design of cementitious materials. This is based on the following:

- Multiscale analysis of biological materials has been widely used by researchers out of necessity to understand the origin of macroscale properties through the complex arrangement of hierarchies at nano- and microscale. This has led to the development of novel techniques for developing and informing computational models using a bottom-up approach. Recent research with cement paste has focused on the nanoscale behavior of the C-S-H building block, and the adaption of methods from the biological community will aid in upscaling current models. Specific examples will be discussed in Section 4.
- The origin of durability in biological materials and cement paste share many similarities, particularly the extrinsic toughening mechanisms which diminish the stress concentrations at crack tips and inhibit crack propagation [28]. Microcracking, crack deflection, and grain bridging are the predominant strengthening mechanisms at the microscale for both bone and cement paste [62, 63]. Furthermore, the shear-compression interlock from roughness and asperities of sliding surfaces that occurs in nacre is also well known in cementitious materials for contacting crack planes loaded in compression or shear [64-66]. In addition to the hierarchies previously discussed, natural materials use carefully tuned interfaces to improve flaw tolerance [67, 68]. The interfacial behavior of cement paste across multiple length scales is a fundamental problem that requires further research, and can seek inspiration from the design principles used by natural materials and the analysis techniques of the biological materials community. These interfaces in cementitious materials include the interfacial transition zone (ITZ) which exists between cement paste and aggregates in bulk concrete [69, 70], as well as interfaces between cement paste and tensile reinforcing such as fiber-reinforced polymers (FRP) [71-74]. Aside from mechanical properties, both bone and cement paste exhibit a

stress-relaxation behavior, or the inverse of creep, which is similar to glassy materials [75, 76]. Therefore, one may expect similar phenomenological behavior under various loading conditions and rates.

- Analogous degradation mechanisms are observed in cementitious materials and bone as shown in **Figure 3**. Cancellous bone, which is commonly known as spongy bone, is responsible for mechanical load distribution in the human body. When osteoporosis occurs, the cancellous bone is severely affected causing decalcification and pore enlargement which leads to cracking of the material (see **Figure 3A**). Construction materials undergo a wide range of physical and chemical exposure from a service environment [77]. Due to this exposure, the physical ingress of soluble salts occurs within the solid cementitious matrix along with leaching of calcium from the dissolution of Portlandite and C-S-H [78, 79]. The leaching of ions from the pore solution is responsible for dissolution of the hydrates and a resulting increase in porosity as shown in **Figure 3B** for a mature cement mortar subjected to accelerated testing [80]. For both osteoporotic bone and leached cementitious materials, the increase in porosity of the mineralized material results in a decrease in stiffness and strength, and increase in permeability.

Fig. 3: Degradation processes in biological and cementitious materials. (A) Comparing healthy bone to osteoporotic bone [Image courtesy of Dr. James Weaver]. (B) Decalcification in a mature Portland Cement mortar when exposed to an ammonium nitrate solution (adapted with permission from [80]). The darkened regions on the treated sample are a result of the leaching of calcium from the material

- Natural systems have a unique ability to form favorable structures through self-assembly processes. This is of particular importance in the modification of cement paste, where self-assembly mechanisms are relatively well understood and can be modified through proper mix design. Because biological materials are typically assembled from the bottom-up, it is often useful to discuss these materials in the context in which they assemble. For examples, diatoms, a form of phytoplankton occurring in the ocean, are able to grow silica shells with complex morphologies despite being present in an aqueous ion filled environment through a unique ion uptake mechanism [81]. Like cement paste, natural materials are susceptible to fluctuations in the chemical and physical environment during the formation and lifetime of the material [82]. However, biological materials are more robust because they are able to remodel and preserve superior properties whereas a cement paste may suffer a drastic reduction in properties from changes in curing conditions. Lessons on the construction of more resilient systems in the presence of additives would lead to more durable infrastructure.
- Natural systems form superior materials using a limited supply of available building blocks and minimal amounts of energy. These systems have been optimized due to millions of years of evolutionary pressures. For cement paste, a large variety of additives are available for mix design to control the nano- and microstructure of cement paste, providing additional degrees of freedom compared to natural materials. However, the selection of the correct proportions of raw material, necessary catalysts, and consideration of embodied energy are currently accomplished through trial and error. The use of locally available resources, such as fly ash or volcanic ash, allows for the replacement of Portland cement to achieve more sustainable materials. In Section 5 of

303 this paper, we introduce an algorithmic framework for the analysis and design of novel
304 cement based materials in the presence of additives to aid in mix design.

305 From the above, it is clear that an understanding of the biological world, and techniques
306 from biological materials science, will allow for the design of improved cement paste materials.
307 The material science community has embraced the bioinspired methodology and begun to
308 redesign processing methods for conventional synthetic materials such that they incorporate the
309 structures that bring success to natural materials. For cement paste, an example of bioinspired
310 design include fiber reinforcements which increases fracture toughness in a manner similar to the
311 fibrils of bone [83]. Another example is polymer cements, where a suitable water-soluble
312 polymer is used to lubricate interfaces between unhydrated cement grains and produce a densely
313 packed and almost impermeable cement paste structure [84]. The polymer acts as a rheological
314 aid for greater control of the microstructure through mechanisms similar to nacre [85]. The self-
315 healing mechanisms of bone has also motivated research into bioinspired cements which use
316 specialized additives or designs to enable the healing of microcracks through mineralization. A
317 variety of approaches have been utilized and were recently reviewed [86]. For enhancing
318 resistance to chemical attack, nanoparticles can be used to densify the microstructure and act as a
319 physical barrier within both bone and cement [87, 88]. More recently, researchers have used
320 alumina platelets which could be positioned and oriented with an external magnetic field to
321 create ordered cement paste composite microstructures [89]. This biomimetic approach led to
322 enhanced stiffness, strength and fracture toughness compared to a plain cement paste and a
323 cement paste composite with a random alumina reinforcement distribution. These examples
324 emphasize the benefits of the selection of additives based on natural design principles to achieve
325 more durable cementitious materials.

Although there has been great success in creating materials which explicitly implements the hierarchies through 3-D printing, sintering, or sol-gel techniques, a different approach is needed for cement paste. Cement paste already has established hierarchies within the hydrated building blocks and pore network. In this case, it is necessary to modify the mix such that desirable mechanisms are embedded within the context of cement paste.

3. Tools for Multiscale Design of Cement Paste

Although cement-based materials have been developed and improved for centuries, recent decades have seen a renaissance in the characterization and modeling of cement paste at subnanometer, nanometer, and micron length scales. This has been driven by modern experimental techniques coupled with progress in computational modeling. These tools have been largely applied to the study of OPC paste materials, but are also appropriate for investigating the role of additives in supplementary cement paste materials. In this section, we will give a brief review of the methodologies used as well as the implications they have on designing cementitious structures. **Figure 4** gives a summary of the dominant length scale and relevant experimental and modeling approaches. Great research efforts have been placed into developing tools for modeling materials across these length scales. In the context of experimental data, such methods provide a framework in which proposed mechanisms can be tested to explain the observed phenomena. By understanding the mechanisms responsible for favorable or unfavorable bulk properties, it becomes possible to design materials that exaggerate such mechanisms and produce a better bulk material.

Fig. 4: Tabulation of modeling and experimental approaches utilized in the description of cement paste. (Left) Modeling techniques range from quantum mechanics based methods at the smallest length scale to continuum length scales. Specific implementations are shown in brackets below each method, and include density function theory (DFT), Hartree-Fock (HF), the reactive force field ReaxFF, the empirical force fields (ClayFF and CSHFF), and finite element analysis (FEA). (Right) Experimental tools for characterizing and describing cement paste.

3.1 Numerical Modeling

Computational models allow for study of the material behavior at length and time scales that are inaccessible to conventional experiments. Simulation also allows for parametric studies of variations in the input properties, such as geometry or mechanical properties, to understand fundamental processes and propose new designs. In this section, we provide a brief description of the computational techniques relevant to multiscale analysis.

As shown in **Figure 4** at the smallest length scales, quantum-mechanical based methods such as density-functional theory (DFT), Hartree-Fock (HF) and quantum Monte Carlo can be

used. These methods consider electrons explicitly which leads to immense computational complexities that limits system size. However, these methods have been used extensively in the field of cement science to understand the fundamental interactions, origin of cohesive forces, and chemical reactions [90-93]. Shahsavari et al. used density functional theory to calculate the elastic constants of Tobermorite and Jennite, which are two minerals that are used as model systems in cement paste [90]. Additionally, these tools have been useful in the study of the reactivity of representative clinker phases with water [94]. By understanding the role of electronic structure in the presence of impurities, strategies could be developed for controlling clinker reactivity and potentially tailoring the performance of cement paste [91, 92]. Fundamental processes including kinetics during the formation, hardening, and aging of cement pastes are governed by chemical interactions between the electrons of atoms.

Although a first-principle approach provides a more detailed description of atomic behavior, the computational complexities limit simulation sizes to thousands of atoms and timescales on the order of picoseconds, making it inaccessible to larger scale phenomena. To address this, methodologies have been developed that simplify the interactions of individual electrons to effective potentials between atoms through molecular dynamics. This simplification drastically speeds up calculations and allows simulations on the scale of tens of nanometers and time scales on the order of nanoseconds, depending on the complexity of the force field and size of the system. Interaction potentials can be classified as reactive or classical. The reactive force field ReaxFF [95] is capable of capturing bond breaking and reformation, allowing for the consideration of fracture [96], electrostatic charge equilibration, and chemical reactions such as water dissociation [60]. These capabilities allow reactive force fields to be utilized as a bridge between first-principles simulations and classical molecular dynamics. Nanoscale behavior

modeled with reactive or classical pair potentials are typically limited to nanosecond simulations, but can be extrapolated over longer time periods through the use of transition state theory techniques. These methods of bridging time scales are further discussed in Section 4.2.

Analogous to the previous simplification from first principles to molecular dynamics, coarse-graining allows for a further reduction of the degrees of freedom to model systems that are too large to describe atomistically, but still too small for continuum behavior. Specific implementations of this approach may involve an adaption of the force field by reducing the complexity of atomic interactions, or the grouping of individual atoms to reduce the overall number of particles. The biological materials community has developed rigorous coarse-graining techniques for modeling hierarchies at larger length scales. These methods have been used to describe the deformation modes and interfacial mechanics of collagen fibril arrays [97] and investigate the role of material hierarchies on the fracture toughness of bioinspired materials [98]. For cement paste, coarse-graining allow for the modeling of building block assemblies on the order of hundreds of nanometers.

The largest length scales considering a cement paste composite may be treated with continuum mechanics techniques. Initial approaches for numerically modeling mechanics of cementitious materials homogenized microstructural details by assuming a characteristic size and distribution of microcracks, with the growth of cracks being represented by the degradation of the material's elastic stiffness [99, 100]. However, a mesoscale analysis requires the explicit consideration of microstructural features to establish structure-property relationships. Numerical approaches that consider discrete microstructures include lattice models or discrete finite element methods (FEM). Lattice models rely on a rigid network of nodes, which may be regularly or randomly placed, that are connected through truss or beam elements [101]. Discrete FEM

models commonly use traditional finite element formulations with mesh boundaries that are described by a traction-separation law to describe the fracture process zone [102, 103]. A more flexible approach for arbitrary cracking patterns is the extended finite element method (XFEM) which is capable of modeling discontinuities in the displacement field along a crack path [104]. For multiscale approaches, the Virtual Internal Bond (VIB) method can be used to couple atomistic interaction potentials with FEM techniques according to the Cauchy-Born rule that assumes atomic deformations follow a continuum description [105, 106]. Variations of the above techniques have been used to investigate macroscopic strength and toughness properties by capturing the dynamics of crack initiation and propagation in a variety of quasi-brittle materials.

3.2 Experimental Characterization

Cement paste has a porous structure containing a mixture of solid phases, each with varying degrees of hydration and crystallinity. The distribution and make-up of these solid phases and pore network are contingent on the mixture of cement binder, additives, water to cement ratio, and external factors like temperature and relative humidity. The complexity and random nature of the cement paste microstructure leads to complications in characterization. Many scientists have not only overcome these barriers, but have also utilized this complexity to make useful measurements about a cement paste's structure.

A complete description of cement paste requires an understanding of not only the heterogeneous hardened microstructure, but also the kinetics controlling the initial microstructure formation and setting behavior. A Venn diagram linking the various experimental techniques used to characterize cement paste over multiple length and time scales is shown in **Figure 5**. Understanding the mechanisms controlling the formation of pore and solid

phases during and after curing of cement paste provides guidelines for the selection of supplementary cementitious materials. It is the arrangement and interaction of these phases within the hardened composite that controls the durable properties of the material. In the following sections we provide a brief review of how the dominant phases present in cement paste mixtures are characterized at multiple length and time scales, and how this information may be included in relevant mesoscale models.

Fig. 5: Experimental techniques that identify the mechanism and transport that can be related to the durability of the cement paste

3.2.1 Solid Phase Characterization

Solid phases in a hardened OPC paste include hydrated gels like C-S-H, mineral phases such as calcium hydroxide, and unhydrated clinker materials. When additives are included, additional hydration products like calcium-alumino-silicate-hydrate (C-A-S-H), magnesium-silicate-hydrate (M-S-H), tetracalcium aluminate hydrate and strätlingite may also form depending on the mix composition and hydration environment [107-110]. Identifying and characterizing this complex arrangement of solid phases within a hydrated cement paste

microstructure requires a combination of experimental techniques. The hydrated gel phase nanostructure of both OPC paste and cement paste with additives continues to be actively discussed in the literature [111-114], and has been recently reviewed [115]. The purpose of this section is to provide a brief overview of how these proposed structural models have been informed by experiments.

At the atomistic scale (~ 1 nm), the current understanding of the fundamental gel phase building block structures were developed through a combination of small-angle scattering techniques (SANS and SAXS), nuclear magnetic resonance (NMR) spectroscopy, and X-ray diffraction (XRD). Small angle scattering experiments allow for the determination of the solid density, chemical composition, and internal water content [59], whereas NMR and XRD can provide quantitative information regarding the atomic structure, such as tetrahedral coordination and atomic spacing [116-119]. Experimental information regarding the atomic structure of individual constituents can be complemented by first principles modeling techniques to evaluate thermodynamically favorable building block structures [90, 120]. One study used computational models to simulate the silicon NMR spectra from DFT models of Tobermorite and Jennite minerals to compare with experimental results for C-S-H [121].

At larger length scales (~ 10 -100 nm), the hydrated gel phase forms a solid-pore composite, with the solid phase consisting of an arrangement of the fundamental layered building block. The particle distributions, shape, and surface/volume fraction of these layered building block assemblies can be quantified through the angular width, intensity and scattering profile obtained from small angle scattering experiments (SANS and SAXS). These studies suggest the grouping of the layered building block into discrete nanoparticles with a brick-like morphology and characteristic length on the order of 5 nm [122, 123]. A study of various simulated solid-

pore particle morphologies suggested that significant polydispersity of the hydrated gel phase was necessary to explain scattering spectra [124]. Synchrotron XRD of synthetic C-S-H has also been used to suggest that the building blocks arrange to form spherical nanocrystal with a diameter of approximately 3.5 nm [125].

For mechanical properties of the hydrated gel phase, nanoindentation has become a powerful technique for characterizing the stiffness and hardness of the solid-pore composite [126]. Constantinides and Ulm showed that nanoindentation can be used to deconvolve the presence of two phases of C-S-H within cement paste, which differ in their porosity and packing efficiency [23, 127]. Furthermore, it has been utilized to probe creep of the nanoscale C-S-H particles as a function of packing density [128]. Nanoindentation measurements can be used to map mechanical properties of a cement paste composite over tens of micron by utilizing the statistical nanoindentation grid techniques developed by Ulm et al. [129]. This provides mechanical information of the heterogeneous composite, including mineral and clinker phases. Combining these methodologies with chemical characterization techniques such as SEM-EDS enable robust mapping of chemo-mechanical properties of cement paste [130].

The cement science community has developed rigorous procedures to image cement paste at various length scales spanning from nm to cm. An understanding of the complex microstructure of cement paste and its susceptibility to internal changes from drying or hydration requires techniques capable of obtaining high-resolution information without disrupting the very material being studied. These standards rely on a series of staged polishing steps, which correspond with the desired length scale for imaging. Back-scattered electron (BSE) imaging has shown to be effective for quantifying the location and combination of phases present in cement paste. Because BSE imaging has brightness, which corresponds with local atomic

density, a great deal of information can be gained. Scrivener [131] and others have improved this technique for the past three decades so that the information can be used over a great multitude of length scales provided that the samples are carefully prepared. Diamond provides a pictorial introduction to this topic [132]. More recently, BSE imaging has been coupled with Energy-dispersive X-ray spectra (EDS) analysis to provide more precise chemical information within a BSE image [133, 134]. Additionally, environmental SEM has enabled observation of the microcracking process from shrinkage and swelling [135-137], as well as the role organic admixtures play on the resulting cement paste. For finer length scales, transmission electron microscopy (TEM) can reveal details about the nanostructure of cement paste [113, 138].

3.2.2 Pore Phase Characterization

Recently, there has been a great emergence of more holistic measurements of cement paste. Because the pores of cement paste occur over a great multitude of length scales, many experimentalists have taken the approach of measuring the entire system simultaneously and later identifying the individual components at each length scale. Juenger and Jennings showed the usage of nitrogen adsorption to characterize the microscopic pore structure of cement paste [139]. More recently it has been shown that water sorption can be used to access pores that are inaccessible by N₂ sorption. In conjunction with NMR relaxometry, these techniques have greatly elucidated multiple mechanisms of water contained in cement paste, and the distribution of pore sizes within the assembled building block structures [140]. Specifically, this has allowed for the characterization of explicit pore hierarchies in the building block assemblies of C-S-H. The smallest interlayer pores are integral to the layered building block structure and less than 1 nm in thickness, gel pores range from 1 to 10 nm and remain because they are too small to be filled by hydrating products, and capillary pores are those larger than 10 nm [26]. The

interactions between the hydrated gel phase and the fluid containing pore network in cementitious materials control properties such as creep and shrinkage [27].

X-Ray microtomography is an emerging technique that has been used for examining porous materials [141]. This method allows for three dimensional characterization of the capillary pore network in hardened cement paste [142]. At these length scales, pores greatly contribute to the overall strength and toughness of the cement paste composite, in addition to the material's permeability. This data has been used to quantify changes in the hydrating phases and pore network with the inclusion of additives [143, 144]. The ability to extract the size, morphology, and connectivity of the pore network allows for the separation of the segmented and effective porosity as shown in **Figure 6**. Segmented porosity is associated with the extracted pore space without any consideration of connectivity, whereas the connected fraction of the whole pore network which is percolating in nature is known as the effective porosity. Effective porosity provides a better indication of a material that is susceptible to transport of harmful chemicals in cement paste. This technique has also been utilized to directly construct two dimensional continuum models of a cementitious composite [145], although three dimensional geometries could also be obtained and has been utilized for studies of bone [146].

Fig. 6: X-Ray microtomography of 28 day cured OPC prepared with 0.45 water to cement ratio
 (A) Gray scale volume, (B) segment porosity, green color is solid and white are the pores (C)
 percolating pore networks (green color refers to solid and white shows the porosity) (Data
 collected at Advanced Photon Source (APS), Argonne National Laboratory)

3.2.3 Microstructure Formation Characterization

The complex processes controlling the setting and hardening of a cement paste microstructure is an area of continued research [147]. Studies have used Quasi-elastic Neutron Scattering (QENS) to characterize the early age kinetics of hydrating cementitious systems [148-150]. QENS tracks the motion of hydrogen atoms, which allows for the detection of the different motions of water in capillary and gel pores. For developing new cement paste mixtures with additives, QENS can evaluate the influence of various mix designs, curing temperatures, and relative humidity (RH) along with variation in the time scale of neutron spectra [151]. This provides detailed information regarding the initial formation of the pore structure at the length scale of the assembled building blocks (~10-100 nm). Recent studies have shown that QENS can also be used to successfully differentiate chemically and physically bound water that can

interact with the surface of the gel pores in the cement paste [148, 152]. Successful calculation of the loss of water can be related to thermal shrinkage that occurs during the exothermic reactions from hydrating gels such as C-S-H. In addition to QENS, inelastic neutron scattering (INS) helps to investigate the movement of atoms by providing detailed information on the vibrational modes of hydrogen on a time scale of less than 10^{-10} seconds [153]. Inelastic neutron spectrometry is commonly used for obtaining high-energy transfer data. The same QENS instrument can also be used to collect INS data appearing in a spectrum that is different from the elastic position.

As a demonstrative study, QENS spectra was collected at multiple times after the initial mixing of an OPC paste with a water to cement ratio of 0.55 as shown in **Figure 7A**. As the hydration process continues, the water changes its state from free to immobile due to the evolution of the cementitious matrix. It is evident that the quasi-elastic component solely comes from the water fraction and has a strong inter-dependence on the scattering vector (Q). Studies show that broadening of the spectrum increases with the increases in Q values [154-157]. The elastic spectrum is indicated by the sharp peak, which lies around zero energy transfer that arises due to fixed or immobile hydrogen fractions, which are involved in the formation of the reaction products such as C-S-H and calcium hydroxide. During the early stages of hydration, the free water is indicated by a broad component of the spectrum due to the presence of mobile hydrogen. **Figure 7B** shows a double Lorentzian and Gaussian model which was fit to the QENS spectra to calculate the Bound-Water-Index (B-W-I) similar to prior studies by Thomas et al. [158]. **Figure 7C** shows how the B-W-I can be used to monitor the hydration process by indicating the conversion of mobile hydrogen present in the free water to immobile hydrogen atoms associated to the chemically bound water in the hydrated material [149]. B-W-I also helps

to predict the induction period that governs the dissolution and nucleation process controlling the type of gels formed during the initial stage of hydration. The B-W-I, in conjunction with small angle scattering data, allows for the determination of coarse or fine gel formation when admixtures such as fly ash, silica fume, natural aluminosilicates, and volcanic ash are used as partial or complete substitution for Portland cement. This also provides insight into the performance of additives that can be used for designing for specific applications such as fast or slow setting cement pastes.

Fig. 7A: QENS spectra obtained on high flux backscattering spectrometer (HFBS) for hydrating cement paste for 10.5 hours prepared with Ordinary Portland Cement (OPC) and 0.55 water to cement ratio. (Data collected at NCNR, National Institute of Standards and Technology). **(B)** Typical fitting of the QENS data at 3 hours of hydration time for IP-50 using DAVE detailing the instrument resolution and Double Lorentzian profiles as dotted lines. The overall fit through the data black solid is indicated by the solid line. **(C)** Bound water index (B-W-I) calculated using a three component model using one Gaussian and two Lorentzians.

4. Exploring the Mesoscale

A mesoscale approach allows for the connection of material structure with bulk engineering properties. For cement paste, macroscale durability originate at multiple scales requiring concurrent multiscale techniques. Based on the complexities within cementitious materials, we distinguish two fundamental problems which require a mesoscale approach, bridging length scales and time scales. The bridging of length scales allows for a bottom-up understanding of structure-property relationships and potentially enables the design of cementitious materials. This approach is necessary to connect lower length scale features with the macroscale stiffness, strength and toughness properties of the overall composite as described in Section 4.1. Many processes in cement paste, such as hydration, shrinkage, creep, and the ingress of harmful chemicals, are dynamic phenomena that originate within nanoscale structures. As a result, a traditional molecular dynamics simulation which is limited to tens of nanoseconds is unable to fully characterize this behavior. Techniques that have been developed to handle these transient problems will be discussed in Section 4.2.

4.1 Bridging Length Scales

The typical numerical modeling techniques and their relevant time and length scales are shown in **Figure 4** and discussed in Section 3.1. Upscaling a model to connect behavior with larger length scale features requires a simplification that retains the physics that are the most essential at the smaller scale. This methodology allows for the bottom-up design and analysis of materials analogous to the hierarchical assembly of biological materials. The complexities of cement paste necessitate this technique to fully understand the influence of chemistry within the fundamental building blocks, the interactions between solid and porous phases in an assembly of building blocks, and the composite response of the complete microstructure.

4.1.1 Building Block (~ 1 nm)

Based on a variety of experimental techniques, including XRD, NMR, and TEM, Pellenq et al. constructed an atomistic model for cement hydrates [159]. This model started with the mineral Tobermorite and systematically manipulated the chemistry by controlling the calcium to silicon ratio and explicitly modeling the presence of water. The result is a layered structure with defective crystalline calcium silicate layers separated by an interface containing water, hydroxyl groups, and calcium ions. Since its introduction, the model has been updated with a reactive force field that is capable of capturing the dissociation of water and balancing of electrostatic charges within the defective structure [60, 120]. This atomistic model has served as the foundation for studies of topology [160], confined water dynamics [161], and mechanical properties [162] as a function of chemical composition and polydispersity of calcium silicate chains [163].

Molecular modeling is also appropriate for investigating the deformation behavior of the many interfaces existing within cementitious materials. Interfacial properties are known to be critical to the macroscopic strength, toughening, and creep behavior of cement-based materials, and this knowledge could be expanded through atomistic models simulating the origin of these cohesive interactions [71, 72, 74, 164]. Researchers could benefit by adopting computational methodologies used to study the inorganic-organic interfaces within biological materials. Steered Molecular Dynamics (SMD) is one approach for isolating the response of interfacial atoms while considering the effects of thermal activation and loading rates. The method is motivated by the force-displacement results obtained through atomic force microscopy (AFM) experiments [165, 166], and has been used to study shear tractions and free energy barriers for protein unbinding and interfacial shear in bone [167]. Another technique is the generalized stacking fault (GSF) approach, which has historically been applied to homogeneous crystalline

metals, but has recently been shown to be effective for studying chemically and spatially complex interfaces. By imposing rigid shear of adjacent calcium silicate layers across the confined water interface in C-S-H, the shear traction-displacement curve and maximum shear stress was obtained while also reducing the coupling between deviatoric and hydrostatic stress components and smoothing stress fluctuations from internal atomic rearrangements [168]. The confined water interface between adjacent C-S-H layers has been well characterized through simulations, but additional research is needed to consider interactions between binder, mineral, and unhydrated phases within the composite. Kalinichev et al. review applications of molecular dynamics in mineral systems involving confined water and makes connections with cement paste [169]. This interfacial behavior is critical to the development of interactions that describe the interactions at larger scales.

The above studies have focused on modeling the behavior of the fundamental building block for the binder phase in OPC pastes. In the presence of additives, additional gel and mineral phases are formed that have received less attention. Additives with high alumina content, like fly ash or volcanic ash, result in the formation of Calcium-Alumina-Silicate-Hydrate (C-A-S-H) gels. Future studies are needed to build on recent work to develop and understand these building blocks that form with supplementary cementitious systems [110, 170-172]. Modeling has identified general trends that are in agreement with NMR experiments and whose implications should be investigated at larger scales. This includes an increase in the mean chain length (MCL) and a more interconnected three dimensional structure (increase in Q_3 and Q_4 coordination) with decreasing Ca/Si ratio for C-A-S-H gels [110, 170, 173].

Although studies of atomic building blocks provide insights on nanoscale behavior which are inaccessible to conventional experiments, the models discussed neglect many features that

contribute to durability of cement paste, such as defects within the microstructure created from gel pores, capillary pores, inefficient particle packing of agglomerated building blocks, and imperfect interfaces between solid phases. As a result, the compressive and tensile strengths of these models are on the order of 10^3 MPa, which is significantly higher than the experimental compressive strength and tensile strengths on the order of 10^2 and 10^1 MPa, respectively. These discrepancies may begin to be resolved by considering the inherent defects within arrangements of layered building blocks.

4.1.2 Assembled Building Blocks (~ 10-100 nm)

Assemblies of building blocks can be constructed according to data regarding the length, shape, and connectivity of the building blocks structures probed through both experiments and computations. This length scale provides a significant and relatively unexplored frontier for continued mesoscale research. These models capture the interfaces between layered building blocks, inclusion of gel pores, and potentially smaller capillary pores. Models thus far have focused on C-S-H which forms in OPC paste, and the consideration of hydrated gels like C-A-S-H that form with additives should be pursued. At this length scale, elastic and inelastic mechanical properties as well as creep behavior predicted through models may be directly compared to nanoindentation experiments.

A fully atomistic study by Dolado et al. investigates the formation of the C-S-H structure within an approximately 10 nm cubic simulation box according to the polymerization of hydrated silica with solvated calcium ions based on a sol-gel type process [174, 175]. The simulation reveals a nanobranched C-S-H structure with a scattering spectra that shows excellent agreement with experimental SANS, NMR, and XRD data. Although no mechanical properties are investigated to compare with nanoindentation experiments, the authors identify the formation

of a $3 \times 3 \times 6 \text{ nm}^3$ ellipsoid within the branched structure that retains features of the proposed building blocks and is close to the size and morphology determined by other small angle scattering and synchrotron XRD studies.

A different approach was adopted by Masoero et al. who developed a colloidal model of C-S-H on the order of 100 nm by considering the polydispersity of spherical nanoparticles ranging from 1 to 10 nm in diameter [176]. The interactions between nanoparticles was based on a simple Lennard-Jones potential that was fit according to the elastic constants and shear strength obtained from simulations of the fundamental building blocks, effectively coarse-graining thousands of atoms into a single nanoparticle. The model has been used to investigate the effect of polydispersity on the packing density of C-S-H grains to reproduce nanoindentation measurements. These studies have also illustrated the changes in mechanical properties compared to the building block models, with various packing configurations resulting in an order of magnitude reduction in shear strength and transition from compacting to dilating behavior under shear deformation [177]. Further improvements on this model could include additional interaction terms or changes to the particle size and shape which greatly affect packing efficiency [178-180]. Future models should strive to reconcile the structural agreement observed by Dolado et al. with the positive trends in mechanical behavior obtained by Masoero et al.

4.1.3 Cement Paste Composite (~ 100 μm)

Models of the cement paste composite allow for the consideration of the largest pores and heterogeneous arrangement of solid phases along with their associated interfaces. These features collectively control the mechanical behavior of the material that are evaluated through macroscale experiments such as compression, flexure, and fracture tests. Continuum-based models such as finite elements require constitutive laws for each solid phase that could be

formulated through lower length scale models. Depending on the size of the model, this may be accomplished through the homogenization of the structural features within the models of gel phase building block assemblies or micromechanics [181]. This approach has been successfully utilized to study bio-inspired composites based on the molecular dynamic stress-strain behavior of nano-porous and bulk silica constituents [182]. Another appealing technique is to directly inform numerical models by characterizing the mechanical properties of individual phases with experiments. This is exemplified by a study on bone which used grid-based indentation techniques with an atomic force microscope (AFM) to capture the elastic-plastic response of individual phases throughout the microstructure [183]. This data was used to inform a finite element model and showed how continuum level mechanical heterogeneities in bones can enhance energy dissipation of the composite. For cement paste, the nanoindentation grid technique provides mechanical information about the overall composite which may be used to identify individual phases if Gaussian frequency distributions are assumed. As shown in **Figure 8**, this mechanical information can be used along with the testing grid to characterize the material microstructure, including the formation of low density (LD), high density (HD), and ultra-high density (UHD) C-S-H [128]. Other studies have used nanoindentation to investigate mechanical properties of critical locations, such as the interfacial transition zone (ITZ) between cement paste and aggregate in concrete [184]. Macroscale properties may be obtained through a micromechanics approach or direct incorporation of the stiffness field into numerical models.

Fig. 8: Microstructural study of a hydrated cement paste using a nanoindentation grid technique [128]. (A) A frequency density of elastic stiffness properties can be used to identify unique phases assuming Gaussian distributions. (B) The phases identified through the deconvolution of frequency distribution may be shown along with the nanoindentation grid to observe characteristics of the cement paste composite.

Lower length scale models can also provide interfacial mechanics, such as a traction-separation law that defines cohesive failure in finite element models. This approach was first developed to study intergranular fracture in polycrystalline aluminum [185], and has since been utilized to study interfacial failure in bone [186, 187] and general composite interfaces with mismatched elastic properties [188]. One application related to the construction and building industry was the characterization of the effect of moisture on the interfacial strength of silica-epoxy interfaces [73, 164]. These methods provide localized mechanical behavior that cannot be obtained through traditional experiments and is critical for the strength and toughness properties of the composite system.

Images of microstructural features of composites have been used to develop continuum computational models. Optical images of the tiling of nacre tablets were used in one study to build an FEA model that observed the origin of strain hardening behavior from shear-compression interlock caused by the macroscopic roughness of stacked layers [53]. For the more broad class of random heterogeneous materials, like cement paste, Torquato and colleagues have developed techniques for numerically reconstructing microstructures according to statistical information obtained from imaging [189]. With this approach, realizations of a multiphase composite are generated which contain the same low-level statistics, such as volume fraction and connectivity, but with locally varying structural details. These local fluctuations have significant implications on the macroscopic response, such as the initiation of material failure at stress concentrations [190]. By sampling a sufficient number of reconstructions, a distribution of effective material properties can be established, allowing for a probabilistic comparison of different random composites. The utility of this approach is reflected in its many applications, with variations being used to model thermal conductivity, fluid permeability, elastic constants, and regions of maximum stress [190-194]. The development of three dimensional reconstruction approaches from a series of two dimensional images allow for more realistic cement paste microstructures [195].

4.2 Bridging Time Scales

A significant challenge in simulation is to extrapolate and predict material behavior based on finite time-scale simulations. Many processes that are essential to the durability of cement paste, including shrinkage, creep, setting and aging, originate at the nanoscale but occur over hours, days and even years. However, the molecular dynamics techniques which are relevant for

these length scales are limited to simulation times on the order of nanoseconds. This section discusses emerging mesoscale approaches for bridging this significant divide.

4.2.1 Creep and Shrinkage

An atomistic system has an energy landscape as a result of potential energy from chemical interactions and kinetic energy from the system temperature. This energy landscape has a distribution of local minima that are separated by saddle points that act as energy barriers for transitions in the system between local minima. The depth of these energy barriers control the system's transient behavior, including its ability to make mechanical, structural, or chemical transitions. A low energy barrier is associated with transitions that occur frequently, such as the translational diffusion of atoms in a liquid or gas. In contrast, large energy barriers lead to more stable configurations, such as the lattice sites of a crystalline solid. **Figure 9** provides a schematic illustrating the topology of an energy landscape for a model material. External factors such as an applied stress field or increase in temperature will modify the energy landscape to impact the likelihood of a system transition [196].

Fig. 9: A schematic representation of an energy landscape for an atomistic system. (A) The potential energy landscape can be viewed as a topographic projection with solid lines indicating

contours of constant energy. The landscape is characterized by local minima separated by saddle points. The Minimum Energy Path (MEP) identifies the lowest energy barriers for a system transition between minima. **(B)** A cross-section of the energy landscape is shown along a MEP. The energy barrier (ΔE) required to transition to an adjacent local minima is shown. The landscape may be altered through external factors such as temperature or stress.

Due to the constraints of molecular dynamics, processes that occur over time scales significantly longer than nanoseconds can be considered as rare events within the accessible simulation time, and therefore would be characterized by larger energy barriers. These processes include the relaxation of stress under a constant external strain field, or the incremental progression of a crack from environmentally assisted processes. A variety of techniques for measuring these energy barriers have been developed, such as steered molecular dynamics (SMD) to evaluate free energy changes along a specified reaction coordinate [165], transition pathway searching algorithms like the nudged elastic band (NEB) which probe for the minimum energy path between an initial and final configuration [197], and metadynamics techniques which more generally measure the entire potential energy landscape to identify local transitions [198]. Transition state theory can then be used to predict the time for the system to overcome the energetic barrier required to perform the specified transition. Although less established than the modeling methods discussed in Section 3.1, it is an emerging and promising field for computational materials science. Transition state theories were recently applied to cement paste at the nanoscale, to investigate creep of both the fundamental building block and arrangement of building blocks [199]. The results indicated that both structures exhibited a logarithmic creep behavior that showed qualitative agreement with nanoindentation experiments [199].

A recent study of reversible shrinkage within C-S-H has examined the role of water existing in different pore environments within the assembly of building blocks [26]. The authors used a continuum analysis which neglected the time-dependence of shrinkage and coupling with

creep behavior, however, a connection was established between microscopic behavior and the macroscopic shrinkage strain of the material. By considering time-dependent behavior from direct molecular dynamic simulations in the future, more detailed analysis could be performed allowing for greater insight on the role of water within nanostructural features of cement paste.

4.2.2 Hydration and Setting

A number of models for the growth and initial hydration behavior of C-S-H have been proposed by considering the length scales at the assembly of building blocks. Instead of transition state theory, researchers have used dimensionless models that are subsequently scaled to compare with experimental data. Colloidal particles, which coarse grain thousands of atoms from the layered building block structure, have been used to investigate the evolution of microstructure and mechanical properties during the precipitation stage of the cement paste hydration process [200-202]. This allows for the consideration of the material as it evolves from a liquid slurry to a solid structure. The C-S-H gel arises via precipitation due to the effective interaction between the hydrates that depends on the original chemical composition of the cement mix. The kinetics are time-dependent and controlled by precipitation which is influenced by the structural relaxation in the C-S-H gels. One model was developed by a combination of Grand Canonical Monte Carlo (GCMC) along with molecular dynamic simulation, and considered colloidal nanoparticles in the range of 1 to 20 nm [201]. The effect of lime concentration on hydration kinetics and morphological evolution of C-S-H gels were captured by observing the acceleration and deceleration regimes. Further understanding is required to consider the effect of additives on the hydration chemistry.

A similar study of aggregating nanoparticles was also performed by Gonzalez-Teresa et al., who considered a time-dependent packing process known as random sequential addition

(RSA) [202]. This model used a hard sphere pair potential which enforces no overlap between colloidal particles, and was able to accurately capture the features of the rate of hydration curve as shown in **Figure 10**. The authors showed that the structure becomes a jammed solid at the maximum growth rate. A different approach was utilized to model the growth of three dimensional C-S-H sheets in order to capture growth rates and morphology within the assembly of building blocks by Etzold et al. [203]. These studies indicate that both spherical and planar kinetic growth models can capture essential features of hydration and setting of cement paste.

Fig. 10: A simulated kinetic growth curve using a random sequential addition algorithm and the corresponding snapshots of the colloidal model at select simulation times. In snapshots, blue particles were initial nucleation sites, pink particles indicate agglomerated beads, and yellow particles indicate those within the initial percolated or rigid structure (obtained with permission from [202]).

A model approach to the characterization of cement paste materials at the micron scale was developed by Bentz and colleagues [204]. Their technique examines a representative microstructure to determine the volume fraction of solid phases, particle size distribution, and chemical composition. This information is used to infer three dimensional structures from a two dimensional image and propose hydration behavior according to cellular automaton (CA) simulations that updates a microstructure based on simple probabilistic rules that represent

complex chemical processes. This approach has allowed for the modeling of changes in elastic constants of OPC microstructures as a function of water to cement ratio, chemical composition, degree of hydration, and simulation cell size [205, 206]. A similar microstructure reconstruction algorithm has also been developed for more general particulate systems [207]. Extending these techniques to supplementary cementitious materials would provide a flexible tool for the design of cement paste.

5. Proposed Multiscale Framework for Cement Paste with Additives

The above sections have shown the capability to combine the existing knowledge and characterization techniques in cement science to that of the multiscale design community to develop and utilize mesoscale models. The hierarchies present in cement paste provide natural transitions through which these fields can be connected. We believe that there is an opportunity to use the success of prior studies on OPC pastes and biological materials to outline a framework that will work more for a broader range of cementitious materials, including those utilizing supplementary cementitious materials.

In order to achieve this, there must be a combination of observables for model building as well as independent model verification. In **Figure 11** we present a framework to perform mesoscale studies at multiple length scales for cement paste materials with additives. This process emphasizes the use of mesoscale models to connect lower length scale features with durable material properties, and is a natural extension of the bottom-up approach commonly employed by biological material systems. Through a feedback of experiment, modeling, and design there can be a transparent framework for improving cement paste.

Fig. 11: Proposed methodology coupling experiments with multiscale computational modeling to understand and design cement-based materials. The use of standardized samples to develop models allows for quantitative comparisons between different mix designs, enabling for a detailed understanding of the role of additives. Modeling allows for investigations of extremes in length and time scales as well as parametric studies of material behavior. By establishing the essential structure-property relationships, new cement paste mixtures may be propped to design novel materials.

In **Figure 11**, the methodology begins with standardized samples that are made according to procedures outlined in appropriate testing standards. Using these standardized samples, we can apply the experimental techniques discussed in Section 3.2 to characterize the material's solid and pore phases at various times after the initial mixing and setting. These methods include microscopy, NMR, small angle scattering, adsorption experiments, and nanoindentation, which provide inputs to models at multiple length scales. The consideration of specimen age allows for a greater understanding of the mechanisms controlling microstructure formation of the dynamic system. From this, a holistic picture of cement paste emerges and we can understand how structure is changed based on the inclusion of additives. Experimental inputs are used to develop

mesoscale models which are specific to the cement paste mixture and curing environment being investigated. Using the mesoscale techniques discussed in Section 4, we can use simulations to determine material properties and establish the critical structure-property relationships. At this stage, we have not only characterized the effect of additives on the structures within cement paste, but have determined the impact on macroscale properties relevant to the design of structures. Simulations are validated with conventional bulk experiments like compression, flexure, fracture and creep tests. Model validation can be done at multiple length scales, such as using nanoindentation stiffness and hardness values to confirm mechanical properties assessed for assemblies of building blocks. Our results would provide a clear structure-property connection, which can be extrapolated over multiple length scales through a bottom-up approach. As an additional step, simulations of the dynamic formation of building block assemblies could be developed using kinetic models and fundamental building blocks. To complete the design loop, we can use lessons learned through experiments and models to propose new cement mix designs.

In summary, by targeting characteristic length scales with established experimental and modeling methodologies in the cement paste and biological materials literature, a greater understanding of the role of additives can be ascertained. The robust framework enables a standardized approach to non-standard mixes. This represents a potential solution to enabling geographic and application tailored cement paste which has great environmental as well as economic potential. These benefits are realized by re-using available waste products from industrial or natural processes as partial or complete replacement for OPC, such as blast-furnace slag from metal refinement, fly ash from coal power plants, and volcanic ash from eruptions.

6. Conclusion

This paper reviews the state-of-the art in cement paste characterization techniques and highlights the importance of multiscale analysis with a particular focus on the mesoscale to understand the origin of durability in hardened cementitious products. The mesoscale provides a critical link between nano- and microscale features with macroscale properties. Establishing these structure-property relationships for cement paste allows for the identification of features at each length scale which improve material performance. Once these details have been identified, innovative materials can be designed to emphasize their benefits. Natural materials have shown that incorporating these design strategies at multiple discrete length scales lead to more durable materials by providing redundancy within their hierarchical structures. This opens exciting new opportunities to innovate cement materials by applying similar bioinspired approaches to engineer the material at multiple length scales and manipulate the self-assembly and setting processes.

In the future, we must build on recent success studying OPC paste materials to enable greater flexibility and control in mix design. To aid in the endeavor, we propose a framework that uses mesoscale science with a combined experimental and multiscale modeling approach to study cement paste in the presence of additives. A detailed understanding of the effect of additives on the solid phases, pore network, and dynamic microstructure formation will allow for the selection of tailored cement paste mixtures. Furthermore, this systematic approach will allow for materials with a lower embodied energy by utilizing locally available raw materials and reducing our reliance on Portland cement. These material innovations will ultimately promote longer-lasting structures and more sustainable cities.

Acknowledgement

This research was conducted within the framework of the MIT-Kuwait Signature Project to connect material innovations with building and city solutions in the context of quantitative sustainability of the built environment. We thank the “Kuwait Foundation for the Advancement of Sciences” and “Kuwait-MIT Center for Natural Resources and the Environment” for the support during this work. Use of the Advanced Photon Source (APS), an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science by Argonne National Laboratory, was supported by the U.S. DOE under Contract No. DE-AC02-06CH11357. This work utilized facilities supported in part by the National Science Foundation under Agreement No. DMR-0944772. We acknowledge the support of the National Institute of Standards and Technology, U.S. Department of Commerce, in providing the neutron research facilities used in this work. We also acknowledge the help of Dr. Carmen Soriano from Argonne National Lab and Dr. Madhusudan Tyagi from NIST for helping Dr. Kunal Kupwade-Patil with Tomography and Quasi Elastic Neutron Scattering data collection and processing. Dr. James Weaver from the Wyss Institute generously provided microscopy images of natural materials that appear within this manuscript.

List of Notations

AFM	: Atomic Force Microscopy
BET	: Brunauer-Emmett-Teller Adsorption
BSE	: Back-Scattered Electron Microscopy
B-W-I	: Bound Water Index
C-A-S-H	: Calcium-Alumino-Silicate-Hydrate
C ₂ S	: Di Calcium Silicate
C ₃ S	: Tri Calcium Silicate
CH	: Calcium Hydroxide
C-S-H	: Calcium-Silicate-Hydrate
DFT	: Density Functional Theory
EDS	: Energy Dispersive Spectrum
EIS	: Electrochemical Impedance Spectroscopy
FEA / FEM	: Finite Element Analysis / Method
FTIR	: Fourier Transform Infrared Spectroscopy
GSF	: Generalized Stacking Fault
H ₂ O	: Water Adsorption
HF	: Hartree-Fock
INS	: Inelastic Neutron Scattering
MD	: Molecular Dynamics
MEP	: Minimum Energy Path
MIP	: Mercury Intrusion Porosimetry
M-S-H	: Magnesium-Silicate-Hydrate
N ₂	: Nitrogen Adsorption
NEB	: Nudged Elastic Band
NMR	: Nuclear Magnetic Resonance
OPC	: Ordinary Portland Cement
Q	: Scattering Vector
QENS	: Quasi-Elastic-Neutron-Scattering

RH	: Relative Humidity
SANS	: Small Angle Neutron Scattering
SAXS	: Small Angle X-ray Scattering
SEM	: Scanning Electron Microscopy
SMD	: Steered Molecular Dynamics
TEM	: Transmission Electron Microscopy
XPS	: X-ray Photoelectron Spectroscopy
XRD	: X-ray Diffraction
XRF	: X-ray Fluorescence Spectroscopy
WAXS	: Wide Angle X-ray Scattering

959

960 **References**

961

- 962 [1] Jackson MD, Moon J, Gotti E, Taylor R, Chae SR, Kunz M, Emwas AH, Meral C, Guttman
963 P, Levitz P. Material and elastic properties of Al-tobermorite in ancient Roman seawater
964 concrete. *Journal of the American Ceramic Society*. 2013;96(8):2598-606.
- 965 [2] Jackson MD, Landis EN, Brune PF, Vitti M, Chen H, Li Q, Kunz M, Wenk H-R, Monteiro
966 PJ, Ingraffea AR. Mechanical resilience and cementitious processes in Imperial Roman
967 architectural mortar. *Proceedings of the National Academy of Sciences*. 2014;111(52):18484-9.
- 968 [3] Sanchez F, Sobolev K. Nanotechnology in concrete—a review. *Construction and Building*
969 *Materials*. 2010;24(11):2060-71.
- 970 [4] Lothenbach B, Scrivener K, Hooton RD. Supplementary cementitious materials. *Cement and*
971 *Concrete Research*. 2011;41(12):1244-56.
- 972 [5] Snellings R, Mertens G, Elsen J. Supplementary Cementitious Materials. *Applied*
973 *Mineralogy of Cement & Concrete*. 2012;74:211-78.
- 974 [6] Schneider M, Romer M, Tschudin M, Bolio H. Sustainable cement production—present and
975 future. *Cement and Concrete Research*. 2011;41(7):642-50.
- 976 [7] Phair JW. Green chemistry for sustainable cement production and use. *Green Chemistry*.
977 2006;8(9):763-80.
- 978 [8] Chindaprasirt P, Jaturapitakkul C, Sinsiri T. Effect of fly ash fineness on compressive
979 strength and pore size of blended cement paste. *Cement and Concrete Composites*.
980 2005;27(4):425-8.
- 981 [9] Bentz DP, Garboczi EJ. Simulation Studies of the Effects of Mineral Admixtures on the
982 Cement Paste-Aggregate Interfacial Zone (SP-105). *ACI Materials Journal*. 1991;88(5).
- 983 [10] Qing Y, Zenan Z, Deyu K, Rongshen C. Influence of nano-SiO₂ addition on properties of
984 hardened cement paste as compared with silica fume. *Construction and Building Materials*.
985 2007;21(3):539-45.
- 986 [11] Chindaprasirt P, Rukzon S, Sirivivatnanon V. Resistance to chloride penetration of blended
987 Portland cement mortar containing palm oil fuel ash, rice husk ash and fly ash. *Construction and*
988 *Building Materials*. 2008;22(5):932-8.
- 989 [12] Chindaprasirt P, Rukzon S. Strength, porosity and corrosion resistance of ternary blend
990 Portland cement, rice husk ash and fly ash mortar. *Construction and Building Materials*.
991 2008;22(8):1601-6.

- [13] Chindaprasirt P, Kanchanda P, Sathonsaowaphak A, Cao H. Sulfate resistance of blended cements containing fly ash and rice husk ash. *Construction and Building Materials*. 2007;21(6):1356-61.
- [14] Monteiro PJM, Kirchheim AP, Chae S, Fischer P, MacDowell AA, Schaible E, Wenk HR. Characterizing the nano and micro structure of concrete to improve its durability. *Cement and Concrete Composites*. 2009;31(8):577-84.
- [15] Mehta PK, Monteiro PJM. *Concrete: microstructure, properties, and materials*: McGraw-Hill; 2006.
- [16] Yip S, Short MP. Multiscale materials modelling at the mesoscale. *Nature materials*. 2013;12(9):774-7.
- [17] Espinosa HD, Rim JE, Barthelat F, Buehler MJ. Merger of structure and material in nacre and bone—Perspectives on de novo biomimetic materials. *Progress in Materials Science*. 2009;54(8):1059-100.
- [18] Gronau G, Krishnaji ST, Kinahan ME, Giesa T, Wong JY, Kaplan DL, Buehler MJ. A review of combined experimental and computational procedures for assessing biopolymer structure–process–property relationships. *Biomaterials*. 2012;33(33):8240-55.
- [19] Mindess S, Young JF, Darwin D. *Concrete*: Prentice Hall; 2003.
- [20] Odler I. *Special Inorganic Cements*: Taylor & Francis; 2003.
- [21] Pellenq RJ-M, Lequeux N, Van Damme H. Engineering the bonding scheme in C–S–H: The ionic-covalent framework. *Cement and Concrete Research*. 2008;38(2):159-74.
- [22] Jennings HM. Refinements to colloid model of C-S-H in cement: CM-II. *Cement and Concrete Research*. 2008;38(3):275-89.
- [23] Constantinides G, Ulm F-J. The nanogranular nature of C–S–H. *Journal of the Mechanics and Physics of Solids*. 2007;55(1):64-90.
- [24] Bishnoi S, Scrivener KL. Studying nucleation and growth kinetics of alite hydration using μ ic. *Cement and Concrete Research*. 2009;39(10):849-60.
- [25] Thomas JJ, Allen AJ, Jennings HM. Hydration kinetics and microstructure development of normal and CaCl_2 -accelerated tricalcium silicate pastes. *The Journal of Physical Chemistry C*. 2009;113(46):19836-44.
- [26] Pinson MB, Masoero E, Bonnaud PA, Manzano H, Ji Q, Yip S, Thomas JJ, Bazant MZ, Van Vliet KJ, Jennings HM. Hysteresis from Multiscale Porosity: Modeling Water Sorption and Shrinkage in Cement Paste. *Physical Review Applied*. 2015;3(6):064009.
- [27] Jennings HM, Bullard JW, Thomas JJ, Andrade JE, Chen JJ, Scherer GW. Characterization and modeling of pores and surfaces in cement paste: correlations to processing and properties. *Journal of Advanced Concrete Technology*. 2008;6(1):5-29.
- [28] Ritchie RO. The conflicts between strength and toughness. *Nature materials*. 2011;10(11):817-22.
- [29] Buehler MJ, Keten S, Ackbarow T. Theoretical and computational hierarchical nanomechanics of protein materials: Deformation and fracture. *Progress in Materials Science*. 2008;53(8):1101-241.
- [30] Gosline J, Lillie M, Carrington E, Guerette P, Ortlepp C, Savage K. Elastic proteins: biological roles and mechanical properties. *Philosophical Transactions of the Royal Society of London Series B-Biological Sciences*. 2002;357(1418):121-32.
- [31] Yeo GC, Aghaei-Ghareh-Bolagh B, Brackenreg EP, Hiob MA, Lee P, Weiss AS. Fabricated Elastin. *Advanced healthcare materials*. 2015;4:2530-56.

- [32] Fratzl P. Collagen: Structure and Mechanics, an Introduction. In: Fratzl P, editor. Collagen. New York: Springer; 2008. p. 1-13.
- [33] Gosline JM, Guerette PA, Ortlepp CS, Savage KN. The mechanical design of spider silks: From fibroin sequence to mechanical function. *J Exp Biol.* 1999;202(23):3295-303.
- [34] Harrington MJ, Gupta HS, Fratzl P, Waite JH. Collagen insulated from tensile damage by domains that unfold reversibly: In situ X-ray investigation of mechanical yield and damage repair in the mussel byssus. *Journal of Structural Biology.* 2009;167(1):47-54.
- [35] Seydel T, Kölln K, Krasnov I, Diddens I, Hauptmann N, Helms G, Ogurreck M, Kang S-G, Koza MM, Müller M. Silkworm Silk under Tensile Strain Investigated by Synchrotron X-ray Diffraction and Neutron Spectroscopy. *Macromolecules.* 2007;40(4):1035-42.
- [36] Keten S, Xu Z, Ihle B, Buehler MJ. Nanoconfinement Controls Stiffness, Strength and Mechanical Toughness of Beta-Sheet Crystals in Silk. *Nature Materials.* 2010;vol. 9(4):359-67.
- [37] Harrington M, Masic A, Holten-Andersen N, Waite JH, Fratzl P. Iron-clad fibers: a metal-based biological strategy for hard flexible coatings. *Science.* 2010;328:216-20.
- [38] Fratzl P, Weinkamer R. Nature's hierarchical materials. *Progress in Materials Science.* 2007;52(8):1263-334.
- [39] Launey ME, Buehler MJ, Ritchie RO. On the Mechanistic Origins of Toughness in Bone. *Annual Review of Materials Research, Vol 40.* 2010;40:25-53.
- [40] Weiner S, Wagner HD. The material bone: Structure mechanical function relations. *Annual Review of Materials Science.* 1998;28:271-98.
- [41] Wang XD, Bank RA, TeKoppele JM, Agrawal CM. The role of collagen in determining bone mechanical properties. *Journal of Orthopaedic Research.* 2001;19(6):1021-6.
- [42] Gao H, Ji B, Jäger IL, Arzt E, Fratzl P. Materials become insensitive to flaws at nanoscale: lessons from nature. *Proceedings of the national Academy of Sciences.* 2003;100(10):5597-600.
- [43] Nalla R, Stölken J, Kinney J, Ritchie R. Fracture in human cortical bone: local fracture criteria and toughening mechanisms. *Journal of biomechanics.* 2005;38(7):1517-25.
- [44] Fratzl P. Bone fracture: When the cracks begin to show. *Nature materials.* 2008;7(8):610-2.
- [45] Katti KS, Katti DR, Pradhan SM, Bhosle A. Platelet interlocks are the key to toughness and strength in nacre. *Journal of Materials Research.* 2005;20(5):1097-100.
- [46] Jackson AP, Vincent JFV, Turner RM. A Physical Model of Nacre. *Composites Science and Technology.* 1989;36(3):255-66.
- [47] Jackson AP, Vincent JFV, Turner RM. The Mechanical Design of Nacre. *Proceedings of the Royal Society Series B-Biological Sciences.* 1988;234(1277):415-40.
- [48] Okumura K. Why is nacre strong? II. Remaining mechanical weakness for cracks propagating along the sheets. *European Physical Journal E.* 2002;7(4):303-10.
- [49] Okumura K, de Gennes PG. Why is nacre strong? Elastic theory and fracture mechanics for biocomposites with stratified structures. *European Physical Journal E.* 2001;4(1):121-7.
- [50] Katti KS, Katti DR. Why is nacre so tough and strong? *Materials Science & Engineering C- Biomimetic and Supramolecular Systems.* 2006;26(8):1317-24.
- [51] Meyers MA, Lin AY-M, Chen P-Y, Muyco J. Mechanical strength of abalone nacre: role of the soft organic layer. *Journal of the Mechanical behavior of biomedical materials.* 2008;1(1):76-85.
- [52] Wang R, Suo Z, Evans A, Yao N, Aksay I. Deformation mechanisms in nacre. *Journal of Materials Research.* 2001;16(09):2485-93.

- [53] Barthelat F, Tang H, Zavattieri PD, Li CM, Espinosa HD. On the mechanics of mother-of-pearl: A key feature in the material hierarchical structure. *Journal of the Mechanics and Physics of Solids*. 2007;55(2):306-37.
- [54] Aizenberg J, Weaver JC, Thanawala MS, Sundar VC, Morse DE, Fratzl P. Skeleton of *Euplectella* sp.: structural hierarchy from the nanoscale to the macroscale. *Science*. 2005;309(5732):275-8.
- [55] Cha JN, Shimizu K, Zhou Y, Christiansen SC, Chmelka BF, Stucky GD, Morse DE. Silicatein filaments and subunits from a marine sponge direct the polymerization of silica and silicones in vitro. *Proceedings of the National Academy of Sciences of the United States of America*. 1999;96(2):361-5.
- [56] Nair AK, Gautieri A, Chang S-W, Buehler MJ. Molecular mechanics of mineralized collagen fibrils in bone. *Nature communications*. 2013;4:1724.
- [57] Wegst UG, Bai H, Saiz E, Tomsia AP, Ritchie RO. Bioinspired structural materials. *Nature materials*. 2014.
- [58] DeVol RT, Sun C-Y, Marcus MA, Coppersmith SN, Myneni SC, Gilbert PU. Nanoscale transforming mineral phases in fresh nacre. *Journal of the American Chemical Society*. 2015;137(41):13325-33.
- [59] Allen AJ, Thomas JJ, Jennings HM. Composition and density of nanoscale calcium–silicate–hydrate in cement. *Nature materials*. 2007;6(4):311-6.
- [60] Manzano H, Moeini S, Marinelli F, van Duin ACT, Ulm F-J, Pellenq RJ-M. Confined Water Dissociation in Microporous Defective Silicates: Mechanism, Dipole Distribution, and Impact on Substrate Properties. *Journal of the American Chemical Society*. 2012;134(4):2208-15.
- [61] Kisailus D, Truong Q, Amemiya Y, Weaver JC, Morse DE. Self-assembled bifunctional surface mimics an enzymatic and templating protein for the synthesis of a metal oxide semiconductor. *Proceedings of the National Academy of Sciences*. 2006;103(15):5652-7.
- [62] Cotterell B, Mai Y-W. Crack growth resistance curve and size effect in the fracture of cement paste. *Journal of materials science*. 1987;22(8):2734-8.
- [63] Wittmann FH, Hu X. Fracture process zone in cementitious materials. *Current Trends in Concrete Fracture Research*: Springer; 1991. p. 3-18.
- [64] Walraven J, Reinhardt H. Theory and experiments on the mechanical behaviour of cracks in plain and reinforced concrete subjected to shear loading. *HERON*, 26 (1A), 1981. 1981.
- [65] Fardis MN, Büyüköztürk O. Shear transfer model for reinforced concrete. *Journal of the Engineering Mechanics Division*. 1979;105(2):255-75.
- [66] Fardis MN, Büyüköztürk O. Shear stiffness of concrete by finite elements. *Journal of the Structural Division*. 1980;106(6):1311-27.
- [67] Fratzl P, Burgert I, Gupta HS. On the role of interface polymers for the mechanics of natural polymeric composites. *Physical Chemistry Chemical Physics*. 2004;6(24):5575-9.
- [68] Ji B, Gao H. Mechanical properties of nanostructure of biological materials. *Journal of the Mechanics and Physics of Solids*. 2004;52(9):1963-90.
- [69] Prokopski G, Halbiniak J. Interfacial transition zone in cementitious materials. *Cement and Concrete Research*. 2000;30(4):579-83.
- [70] Scrivener KL, Crumbie AK, Laugesen P. The interfacial transition zone (ITZ) between cement paste and aggregate in concrete. *Interface Science*. 2004;12(4):411-21.
- [71] Lau D, Büyüköztürk O. Fracture characterization of concrete/epoxy interface affected by moisture. *Mechanics of Materials*. 2010;42(12):1031-42.

1127 [72] Büyüköztürk O, Buehler MJ, Lau D, Tuakta C. Structural solution using molecular
1128 dynamics: Fundamentals and a case study of epoxy-silica interface. *International Journal of*
1129 *Solids and Structures*. 2011;48(14):2131-40.

1130 [73] Lau D, Büyüköztürk O, Buehler MJ. Characterization of the intrinsic strength between
1131 epoxy and silica using a multiscale approach. *Journal of Materials Research*. 2012;27(14):1787-
1132 96.

1133 [74] Gunes O, Lau D, Tuakta C, Büyüköztürk O. Ductility of FRP-concrete systems:
1134 Investigations at different length scales. *Construction and Building Materials*. 2013;49:915-25.

1135 [75] Vichit-Vadakan W, Scherer GW. Measuring permeability and stress relaxation of young
1136 cement paste by beam bending. *Cement and concrete research*. 2003;33(12):1925-32.

1137 [76] Sasaki N, Nakayama Y, Yoshikawa M, Enyo A. Stress relaxation function of bone and bone
1138 collagen. *Journal of biomechanics*. 1993;26(12):1369-76.

1139 [77] Alexander M, Bertron A, De Belie N. Performance of Cement-Based Materials in
1140 Aggressive Aqueous Environments: State-of-the-Art Report, RILEM TC 211 - PAE: Springer
1141 Netherlands; 2012.

1142 [78] Glasser FP, Marchand J, Samson E. Durability of concrete — Degradation phenomena
1143 involving detrimental chemical reactions. *Cement and Concrete Research*. 2008;38(2):226-46.

1144 [79] Dow C, Glasser FP. Calcium carbonate efflorescence on Portland cement and building
1145 materials. *Cement and Concrete Research*. 2003;33(1):147-54.

1146 [80] Burlion N, Bernard D, Chen D. X-ray microtomography: application to microstructure
1147 analysis of a cementitious material during leaching process. *Cement and Concrete Research*.
1148 2006;36(2):346-57.

1149 [81] Hutchins DA, Bruland KW. Iron-limited diatom growth and Si : N uptake ratios in a coastal
1150 upwelling regime. *Nature*. 1998;393(6685):561-4.

1151 [82] Mann S. The chemistry of form. *Angewandte Chemie International Edition*.
1152 2000;39(19):3392-406.

1153 [83] Li VC, Leung CK. Steady-state and multiple cracking of short random fiber composites.
1154 *Journal of Engineering Mechanics*. 1992;118(11):2246-64.

1155 [84] Birchall J. Cement in the Context of New Materials for an Energy-Expensive Future.
1156 *Philosophical Transactions of the Royal Society of London A: Mathematical, Physical and*
1157 *Engineering Sciences*. 1983;310(1511):31-42.

1158 [85] Jackson A, Vincent J, Turner R. Comparison of nacre with other ceramic composites.
1159 *Journal of Materials Science*. 1990;25(7):3173-8.

1160 [86] Wu M, Johannesson B, Geiker M. A review: Self-healing in cementitious materials and
1161 engineered cementitious composite as a self-healing material. *Construction and Building*
1162 *Materials*. 2012;28(1):571-83.

1163 [87] Musham D. Strengthening of Bone Using Electrokinetic Transport of Suspended Calcium
1164 Phosphate Particles. Ruston, LA: Louisiana Tech University; 2010.

1165 [88] Kupwade-Patil K, Cardenas HE. Electrokinetic nanoparticle treatment for corrosion
1166 remediation on simulated reinforced bridge deck. *Journal of nanoparticle research*. 2013;15(9):1-
1167 16.

1168 [89] Carnelli D, Libanori R, Feichtenschlager B, Nicoleau L, Albrecht G, Studart AR. Cement-
1169 based composites reinforced with localized and magnetically oriented Al₂O₃ microplatelets.
1170 *Cement and Concrete Research*. 2015;78:245-51.

1171 [90] Shahsavari R, Buehler MJ, Pellenq RJ-M, Ulm F-J. First-Principles Study of Elastic
 1172 Constants and Interlayer Interactions of Complex Hydrated Oxides: Case Study of Tobermorite
 1173 and Jennite. *Journal of the American Ceramic Society*. 2009;92(10):2323-30.
 1174 [91] Manzano H, Durgun E, Qomi MJA, Ulm F-J, Pellenq RJ-M, Grossman JC. Impact of
 1175 Chemical Impurities on the Crystalline Cement Clinker Phases Determined by Atomistic
 1176 Simulations. *Crystal Growth & Design*. 2011;11(7):2964-72.
 1177 [92] Durgun E, Manzano H, Pellenq RJ-M, Grossman JC. Understanding and Controlling the
 1178 Reactivity of the Calcium Silicate phases from First Principles. *Chemistry of Materials*.
 1179 2012;24(7):1262-7.
 1180 [93] Manzano H, Dolado JS, Ayuela A. Structural, mechanical, and reactivity properties of
 1181 tricalcium aluminate using first-principles calculations. *Journal of the American Ceramic*
 1182 *Society*. 2009;92(4):897-902.
 1183 [94] Durgun E, Manzano H, Kumar PV, Grossman JC. The Characterization, Stability, and
 1184 Reactivity of Synthetic Calcium Silicate Surfaces from First Principles. *Journal of Physical*
 1185 *Chemistry C*. 2014;118(28):15214-9.
 1186 [95] Van Duin AC, Dasgupta S, Lorant F, Goddard WA. ReaxFF: a reactive force field for
 1187 hydrocarbons. *The Journal of Physical Chemistry A*. 2001;105(41):9396-409.
 1188 [96] Buehler MJ, van Duin AC, Goddard III WA. Multiparadigm modeling of dynamical crack
 1189 propagation in silicon using a reactive force field. *Physical review letters*. 2006;96(9):095505.
 1190 [97] Buehler MJ. Nature designs tough collagen: explaining the nanostructure of collagen fibrils.
 1191 *Proceedings of the National Academy of Sciences*. 2006;103(33):12285-90.
 1192 [98] Sen D, Buehler MJ. Structural hierarchies define toughness and defect-tolerance despite
 1193 simple and mechanically inferior brittle building blocks. *Scientific reports*. 2011;1.
 1194 [99] Hillerborg A, Modr M, Petersson P-E. Analysis of crack formation and crack growth in
 1195 concrete by means of fracture mechanics and finite elements. *Cement and concrete research*.
 1196 1976;6(6):773-81.
 1197 [100] Baant ZP, Oh BH. Crack band theory for fracture of concrete. *Matriaux et construction*.
 1198 1983;16(3):155-77.
 1199 [101] Ostoja-Starzewski M. Lattice models in micromechanics. *Applied Mechanics Reviews*.
 1200 2002;55(1):35-60.
 1201 [102] Xu X-P, Needleman A. Numerical simulations of fast crack growth in brittle solids.
 1202 *Journal of the Mechanics and Physics of Solids*. 1994;42(9):1397-434.
 1203 [103] Camacho GT, Ortiz M. Computational modelling of impact damage in brittle materials.
 1204 *International Journal of Solids and Structures*. 1996;33(20):2899-938.
 1205 [104] Mos N, Belytschko T. Extended finite element method for cohesive crack growth.
 1206 *Engineering fracture mechanics*. 2002;69(7):813-33.
 1207 [105] Gao H, Klein P. Numerical simulation of crack growth in an isotropic solid with
 1208 randomized internal cohesive bonds. *Journal of the Mechanics and Physics of Solids*.
 1209 1998;46(2):187-218.
 1210 [106] Ji B, Gao H. A study of fracture mechanisms in biological nano-composites via the virtual
 1211 internal bond model. *Materials Science and Engineering: A*. 2004;366(1):96-103.
 1212 [107] Garcia-Lodeiro I, Palomo A, Fernndez-Jimnez A, Macphee DE. Compatibility studies
 1213 between N-A-S-H and C-A-S-H gels. Study in the ternary diagram Na₂O–CaO–Al₂O₃–SiO₂–
 1214 H₂O. *Cement and Concrete Research*. 2011;41(9):923-31.

1215 [108] Zhang T, Vandeperre LJ, Cheeseman CR. Formation of magnesium silicate hydrate (M-S-
1216 H) cement pastes using sodium hexametaphosphate. *Cement and Concrete Research*. 2014;65:8-
1217 14.

1218 [109] Bernal SA, Provis JL. Durability of Alkali-Activated Materials: Progress and Perspectives.
1219 *Journal of the American Ceramic Society*. 2014;97(4):997-1008.

1220 [110] Puertas F, Palacios M, Manzano H, Dolado J, Rico A, Rodríguez J. A model for the CASH
1221 gel formed in alkali-activated slag cements. *Journal of the European Ceramic Society*.
1222 2011;31(12):2043-56.

1223 [111] Richardson I. Tobermorite/jennite-and tobermorite/calcium hydroxide-based models for
1224 the structure of CSH: applicability to hardened pastes of tricalcium silicate, β -dicalcium silicate,
1225 Portland cement, and blends of Portland cement with blast-furnace slag, metakaolin, or silica
1226 fume. *Cement and Concrete Research*. 2004;34(9):1733-77.

1227 [112] Nonat A. The structure and stoichiometry of CSH. *Cement and Concrete Research*.
1228 2004;34(9):1521-8.

1229 [113] Richardson IG. The calcium silicate hydrates. *Cement and Concrete Research*.
1230 2008;38(2):137-58.

1231 [114] Richardson IG. Model structures for C-(A)-SH (I). *Structural Science*. 2014;70(6):903-23.

1232 [115] Papatzani S, Paine K, Calabria-Holley J. A comprehensive review of the models on the
1233 nanostructure of calcium silicate hydrates. *Construction and Building Materials*. 2015;74:219-34.

1234 [116] Cong X, Kirkpatrick RJ. ²⁹Si MAS NMR study of the structure of calcium silicate
1235 hydrate. *Advanced Cement Based Materials*. 1996;3(3):144-56.

1236 [117] Chen JJ, Thomas JJ, Taylor HF, Jennings HM. Solubility and structure of calcium silicate
1237 hydrate. *Cement and Concrete Research*. 2004;34(9):1499-519.

1238 [118] Richardson IG, Brough AR, Brydson R, Groves GW, Dobson CM. Location of aluminum
1239 in substituted calcium silicate hydrate (C-S-H) gels as determined by ²⁹Si and ²⁷Al NMR and
1240 EELS. *Journal of the American Ceramic Society*. 1993;76(9):2285-8.

1241 [119] Yu P, Kirkpatrick RJ, Poe B, McMillan PF, Cong X. Structure of calcium silicate hydrate
1242 (C-S-H): Near-, Mid-, and Far-infrared spectroscopy. *Journal of the American Ceramic Society*.
1243 1999;82(3):742-8.

1244 [120] Manzano H, Pellenq RJ-M, Ulm F-J, Buehler MJ, van Duin ACT. Hydration of Calcium
1245 Oxide Surface Predicted by Reactive Force Field Molecular Dynamics. *Langmuir*.
1246 2012;28(9):4187-97.

1247 [121] Rejmak P, Dolado JS, Stott MJ, Ayuela A. ²⁹Si NMR in cement: a theoretical study on
1248 calcium silicate hydrates. *The Journal of Physical Chemistry C*. 2012;116(17):9755-61.

1249 [122] Allen AJ, Thomas JJ. Analysis of C-S-H gel and cement paste by small-angle neutron
1250 scattering. *Cement and Concrete Research*. 2007;37(3):319-24.

1251 [123] Chiang W-S, Fratini E, Baglioni P, Liu D, Chen S-H. Microstructure determination of
1252 calcium-silicate-hydrate globules by small-angle neutron scattering. *The Journal of Physical
1253 Chemistry C*. 2012;116(8):5055-61.

1254 [124] Brisard S, Levitz P. Small-angle scattering of dense, polydisperse granular porous media:
1255 Computation free of size effects. *Physical Review E*. 2013;87(1):013305.

1256 [125] Skinner LB, Chae SR, Benmore CJ, Wenk HR, Monteiro PJM. Nanostructure of calcium
1257 silicate hydrates in cements. *Physical review letters*. 2010;104(19):195502.

1258 [126] Hu C, Li Z. A review on the mechanical properties of cement-based materials measured by
1259 nanoindentation. *Construction and Building Materials*. 2015;90:80-90.

- [127] Constantinides G, Ulm F-J. The effect of two types of CSH on the elasticity of cement-based materials: Results from nanoindentation and micromechanical modeling. *Cement and concrete research*. 2004;34(1):67-80.
- [128] Vandamme M, Ulm F-J, Fonollosa P. Nanogranular packing of C-S-H at substoichiometric conditions. *Cement and Concrete Research*. 2010;40(1):14-26.
- [129] Ulm F-J, Vandamme M, Bobko C, Alberto Ortega J, Tai K, Ortiz C. Statistical indentation techniques for hydrated nanocomposites: concrete, bone, and shale. *Journal of the American Ceramic Society*. 2007;90(9):2677-92.
- [130] Chen JJ, Sorelli L, Vandamme M, Ulm F-J, Chanvillard G. A Coupled Nanoindentation/SEM-EDS Study on Low Water/Cement Ratio Portland Cement Paste: Evidence for C-S-H/Ca(OH)(2) Nanocomposites. *Journal of the American Ceramic Society*. 2010;93(5):1484-93.
- [131] Scrivener KL. Backscattered electron imaging of cementitious microstructures: understanding and quantification. *Cement & Concrete Composites*. 2004;26(8):935-45.
- [132] Diamond S. The microstructure of cement paste and concrete - a visual primer. *Cement & Concrete Composites*. 2004;26(8):919-33.
- [133] Sanchez F, Ince C. Microstructure and macroscopic properties of hybrid carbon nanofiber/silica fume cement composites. *Composites Science and Technology*. 2009;69(7-8):1310-8.
- [134] Fernández-Jiménez A, Palomo A, Criado M. Microstructure development of alkali-activated fly ash cement: a descriptive model. *Cement and Concrete Research*. 2005;35(6):1204-9.
- [135] Kjellsen KO, Jennings HM. Observations of microcracking in cement paste upon drying and rewetting by environmental scanning electron microscopy. *Advanced Cement Based Materials*. 1996;3(1):14-9.
- [136] Bisschop J, van Mier JGM. How to study drying shrinkage microcracking in cement-based materials using optical and scanning electron microscopy? *Cement and Concrete Research*. 2002;32(2):279-87.
- [137] Fonseca PC, Jennings HM. The effect of drying on early-age morphology of C-S-H as observed in environmental SEM. *Cement and Concrete Research*. 2010;40(12):1673-80.
- [138] Zhang XZ, Chang WY, Zhang TJ, Ong CK. Nanostructure of calcium silicate hydrate gels in cement paste. *Journal of the American Ceramic Society*. 2000;83(10):2600-4.
- [139] Garci Juenger MC, Jennings HM. The use of nitrogen adsorption to assess the microstructure of cement paste. *Cement and Concrete Research*. 2001;31(6):883-92.
- [140] Muller AC, Scrivener KL, Gajewicz AM, McDonald PJ. Densification of C-S-H measured by ¹H NMR relaxometry. *The Journal of Physical Chemistry C*. 2012;117(1):403-12.
- [141] Ketcham RA, Carlson WD. Acquisition, optimization and interpretation of X-ray computed tomographic imagery: applications to the geosciences. *Computers & Geosciences*. 2001;27(4):381-400.
- [142] Gallucci E, Scrivener K, Groso A, Stampanoni M, Margaritondo G. 3D experimental investigation of the microstructure of cement pastes using synchrotron X-ray microtomography (μCT). *Cement and Concrete Research*. 2007;37(3):360-8.
- [143] Provis JL, Myers RJ, White CE, Rose V, van Deventer JSJ. X-ray microtomography shows pore structure and tortuosity in alkali-activated binders. *Cement and Concrete Research*. 2012;42(6):855-64.

1305 [144] Provis JL, Rose V, Winarski RP, van Deventer JSJ. Hard X-ray nanotomography of
 1306 amorphous aluminosilicate cements. *Scripta Materialia*. 2011;65(4):316-9.
 1307 [145] Rougelot T, Burlion N, Bernard D, Skoczylas F. About microcracking due to leaching in
 1308 cementitious composites: X-ray microtomography description and numerical approach. *Cement*
 1309 *and Concrete Research*. 2010;40(2):271-83.
 1310 [146] Ulrich D, Van Rietbergen B, Laib A, Rueggsegger P. The ability of three-dimensional
 1311 structural indices to reflect mechanical aspects of trabecular bone. *Bone*. 1999;25(1):55-60.
 1312 [147] Bullard JW, Jennings HM, Livingston RA, Nonat A, Scherer GW, Schweitzer JS,
 1313 Scrivener KL, Thomas JJ. Mechanisms of cement hydration. *Cement and Concrete Research*.
 1314 2011;41(12):1208-23.
 1315 [148] Peterson VK, Neumann DA, Livingston RA. Inelastic neutron scattering investigation of
 1316 hydrating tricalcium and dicalcium silicate mixture pastes: $\text{Ca}(\text{OH})_2$ formation and evolution of
 1317 strength. *Journal of Materials Research*. 2006;21(7):1836-42.
 1318 [149] Peterson VK. Studying the hydration of cement systems in real-time using quasielastic and
 1319 inelastic neutron scattering. *Studying Kinetics with Neutrons*: Springer; 2010. p. 19-75.
 1320 [150] Gutberlet T, Hilbig H, Beddoe R, Lohstroh W. New insights into water bonding during
 1321 early tricalcium silicate hydration with quasielastic neutron scattering. *Cement and Concrete*
 1322 *Research*. 2013;51:104-8.
 1323 [151] Bordallo HN, Aldridge LP, Fouquet P, Pardo LC, Unruh T, Wuttke J, Yokaichiya F.
 1324 Hindered water motions in hardened cement pastes investigated over broad time and length
 1325 scales. *ACS Applied Materials & Interfaces*. 2009;1(10):2154-62.
 1326 [152] Allen A, McLaughlin J, Neumann D, Livingston R. In situ quasi-elastic scattering
 1327 characterization of particle size effects on the hydration of tricalcium silicate. *Journal of*
 1328 *Materials Research*. 2004;19(11):3242-54.
 1329 [153] White CE, Provis JL, Proffen T, Riley DP, van Deventer JS. Density functional modeling
 1330 of the local structure of kaolinite subjected to thermal dehydroxylation. *The Journal of Physical*
 1331 *Chemistry A*. 2010;114(14):4988-96.
 1332 [154] Fratini E, Chen S-H, Baglioni P. Investigation of the Temporal Evolution of Translational
 1333 Dynamics of Water Molecules in Hydrated Calcium Aluminate Pastes. *The Journal of Physical*
 1334 *Chemistry B*. 2003;107(37):10057-62.
 1335 [155] Fratini E, Chen S-H, Baglioni P, Bellissent-Funel M-C. Quasi-Elastic Neutron Scattering
 1336 Study of Translational Dynamics of Hydration Water in Tricalcium Silicate. *The Journal of*
 1337 *Physical Chemistry B*. 2002;106(1):158-66.
 1338 [156] Fratini E, Faraone A, Ridi F, Chen S-H, Baglioni P. Hydration Water Dynamics in
 1339 Tricalcium Silicate Pastes by Time-Resolved Incoherent Elastic Neutron Scattering. *The Journal*
 1340 *of Physical Chemistry C*. 2013;117(14):7358-64.
 1341 [157] Ridi F, Luciani P, Fratini E, Baglioni P. Water Confined in Cement Pastes as a Probe of
 1342 Cement Microstructure Evolution. *The Journal of Physical Chemistry B*. 2009;113(10):3080-7.
 1343 [158] Thomas JJ, FitzGerald SA, Neumann DA, Livingston RA. State of Water in Hydrating
 1344 Tricalcium Silicate and Portland Cement Pastes as Measured by Quasi-Elastic Neutron
 1345 Scattering. *Journal of the American Ceramic Society*. 2001;84(8):1811-6.
 1346 [159] Pellenq RJ-M, Kushima A, Shahsavari R, Van Vliet KJ, Buehler MJ, Yip S, Ulm F-J. A
 1347 realistic molecular model of cement hydrates. *Proceedings of the National Academy of Sciences*
 1348 *of the United States of America*. 2009;106(38):16102-7.
 1349 [160] Bauchy M, Qomi MA, Ulm F-J, Pellenq RJ-M. Order and disorder in calcium–silicate–
 1350 hydrate. *The Journal of chemical physics*. 2014;140(21):214503.

1351 [161] Youssef M, Pellenq RJ-M, Yildiz B. Glassy nature of water in an ultraconfining disordered
 1352 material: the case of calcium–silicate–hydrate. *Journal of the American Chemical Society*.
 1353 2011;133(8):2499-510.
 1354 [162] Manzano H, Masoero E, Lopez-Arbeloa I, Jennings HM. Shear deformations in calcium
 1355 silicate hydrates. *Soft Matter*. 2013;9(30):7333-41.
 1356 [163] Qomi MJA, Krakowiak KJ, Bauchy M, Stewart KL, Shahsavari R, Jagannathan D,
 1357 Brommer DB, Baronnet A, Buehler MJ, Yip S, Ulm F-J, Van Vliet KJ, Pellenq RJ-M.
 1358 Combinatorial molecular optimization of cement hydrates. *Nature Communications*. 2014;5.
 1359 [164] Lau D, Broderick K, Buehler MJ, Büyüköztürk O. A robust nanoscale experimental
 1360 quantification of fracture energy in a bilayer material system. *Proceedings of the National*
 1361 *Academy of Sciences*. 2014;111(33):11990-5.
 1362 [165] Izrailev S, Stepaniants S, Balsera M, Oono Y, Schulten K. Molecular dynamics study of
 1363 unbinding of the avidin-biotin complex. *Biophysical journal*. 1997;72(4):1568.
 1364 [166] Hummer G, Szabo A. Free energy reconstruction from nonequilibrium single-molecule
 1365 pulling experiments. *Proceedings of the National Academy of Sciences*. 2001;98(7):3658-61.
 1366 [167] Qu T, Verma D, Shahidi M, Pichler B, Hellmich C, Tomar V. Mechanics of organic-
 1367 inorganic biointerfaces—Implications for strength and creep properties. *MRS Bulletin*.
 1368 2015;40(04):349-58.
 1369 [168] Palkovic SD, Moeini S, Yip S, Büyüköztürk O. Mechanical behavior of a composite
 1370 interface: Calcium-silicate-hydrates. *Journal of Applied Physics*. 2015;118(3):034305.
 1371 [169] Kalinichev AG, Wang JW, Kirkpatrick RJ. Molecular dynamics modeling of the structure,
 1372 dynamics and energetics of mineral-water interfaces: Application to cement materials. *Cement*
 1373 *and Concrete Research*. 2007;37(3):337-47.
 1374 [170] Abdolhosseini Qomi MJ, Ulm F-J, Pellenq RJ-M. Evidence on the Dual Nature of
 1375 Aluminum in the Calcium-Silicate-Hydrates Based on Atomistic Simulations. *Journal of the*
 1376 *American Ceramic Society*. 2012;95(3):1128-37.
 1377 [171] Myers RJ, Bernal SA, San Nicolas R, Provis JL. Generalized structural description of
 1378 calcium–sodium aluminosilicate hydrate gels: the cross-linked substituted tobermorite model.
 1379 *Langmuir*. 2013;29(17):5294-306.
 1380 [172] Hou D, Li Z, Zhao T. Reactive force field simulation on polymerization and hydrolytic
 1381 reactions in calcium aluminate silicate hydrate (C–A–S–H) gel: structure, dynamics and
 1382 mechanical properties. *RSC Advances*. 2015;5(1):448-61.
 1383 [173] Manzano H, Dolado J, Griebel M, Hamaekers J. A molecular dynamics study of the
 1384 aluminosilicate chains structure in Al-rich calcium silicate hydrated (C–S–H) gels. *physica status*
 1385 *solidi (a)*. 2008;205(6):1324-9.
 1386 [174] Dolado JS, Griebel M, Hamaekers J. A molecular dynamic study of cementitious calcium
 1387 silicate hydrate (C–S–H) gels. *Journal of the American Ceramic Society*. 2007;90(12):3938-42.
 1388 [175] Dolado JS, Griebel M, Hamaekers J, Heber F. The nano-branched structure of
 1389 cementitious calcium–silicate–hydrate gel. *Journal of Materials Chemistry*. 2011;21(12):4445-9.
 1390 [176] Masoero E, Del Gado E, Pellenq RJ-M, Ulm F-J, Yip S. Nanostructure and nanomechanics
 1391 of cement: polydisperse colloidal packing. *Physical review letters*. 2012;109(15):155503.
 1392 [177] Masoero E, Del Gado E, Pellenq RJ-M, Yip S, Ulm F-J. Nano-scale mechanics of colloidal
 1393 C–S–H gels. *Soft matter*. 2014;10(3):491-9.
 1394 [178] Torquato S, Stillinger F. Multiplicity of generation, selection, and classification procedures
 1395 for jammed hard-particle packings. *The Journal of Physical Chemistry B*. 2001;105(47):11849-
 1396 53.

1397 [179] Kansal AR, Torquato S, Stillinger FH. Diversity of order and densities in jammed hard-
 1398 particle packings. *Physical Review E*. 2002;66(4):041109.
 1399 [180] Torquato S, Stillinger FH. Jammed hard-particle packings: From Kepler to Bernal and
 1400 beyond. *Reviews of modern physics*. 2010;82(3):2633.
 1401 [181] Ulm F-J, Constantinides G, Heukamp F. Is concrete a poromechanics materials?—A
 1402 multiscale investigation of poroelastic properties. *Materials and structures*. 2004;37(1):43-58.
 1403 [182] Dimas LS, Buehler MJ. Influence of geometry on mechanical properties of bio-inspired
 1404 silica-based hierarchical materials. *Bioinspiration & biomimetics*. 2012;7(3):036024.
 1405 [183] Tai K, Dao M, Suresh S, Palazoglu A, Ortiz C. Nanoscale heterogeneity promotes energy
 1406 dissipation in bone. *Nature materials*. 2007;6(6):454-62.
 1407 [184] Trtik P, Bartos P. Micromechanical properties of cementitious composites. *Materials and*
 1408 *Structures*. 1999;32(5):388-93.
 1409 [185] Yamakov V, Saether E, Phillips D, Glaessgen E. Molecular-dynamics simulation-based
 1410 cohesive zone representation of intergranular fracture processes in aluminum. *Journal of the*
 1411 *Mechanics and Physics of Solids*. 2006;54(9):1899-928.
 1412 [186] Dubey DK, Tomar V. Microstructure dependent dynamic fracture analyses of trabecular
 1413 bone based on nascent bone atomistic simulations. *Mechanics Research Communications*.
 1414 2008;35(1):24-31.
 1415 [187] Luo Q, Nakade R, Dong X, Rong Q, Wang X. Effect of mineral–collagen interfacial
 1416 behavior on the microdamage progression in bone using a probabilistic cohesive finite element
 1417 model. *Journal of the mechanical behavior of biomedical materials*. 2011;4(7):943-52.
 1418 [188] Zhou X, Moody N, Jones R, Zimmerman J, Reedy E. Molecular-dynamics-based cohesive
 1419 zone law for brittle interfacial fracture under mixed loading conditions: Effects of elastic
 1420 constant mismatch. *Acta Materialia*. 2009;57(16):4671-86.
 1421 [189] Torquato S. *Random heterogeneous materials: microstructure and macroscopic properties*:
 1422 Springer Science & Business Media; 2013.
 1423 [190] Kumar H, Briant C, Curtin W. Using microstructure reconstruction to model mechanical
 1424 behavior in complex microstructures. *Mechanics of Materials*. 2006;38(8):818-32.
 1425 [191] Wang M, Wang J, Pan N, Chen S. Mesoscopic predictions of the effective thermal
 1426 conductivity for microscale random porous media. *Physical Review E*. 2007;75(3):036702.
 1427 [192] Torquato S. *Random heterogeneous media: microstructure and improved bounds on*
 1428 *effective properties*. *Applied mechanics reviews*. 1991;44(2):37-76.
 1429 [193] Kanit T, Forest S, Galliet I, Mounoury V, Jeulin D. Determination of the size of the
 1430 representative volume element for random composites: statistical and numerical approach.
 1431 *International Journal of solids and structures*. 2003;40(13):3647-79.
 1432 [194] Torquato S, Pham D. Optimal bounds on the trapping constant and permeability of porous
 1433 media. *Physical review letters*. 2004;92(25):255505.
 1434 [195] Yeong C, Torquato S. Reconstructing random media. II. Three-dimensional media from
 1435 two-dimensional cuts. *Physical Review E*. 1998;58(1):224.
 1436 [196] Malandro DL, Lacks DJ. Relationships of shear-induced changes in the potential energy
 1437 landscape to the mechanical properties of ductile glasses. *The Journal of chemical physics*.
 1438 1999;110(9):4593-601.
 1439 [197] Henkelman G, Uberuaga BP, Jónsson H. A climbing image nudged elastic band method
 1440 for finding saddle points and minimum energy paths. *The Journal of chemical physics*.
 1441 2000;113(22):9901-4.

- [198] Laio A, Gervasio FL. Metadynamics: a method to simulate rare events and reconstruct the free energy in biophysics, chemistry and material science. *Reports on Progress in Physics*. 2008;71(12):126601.
- [199] Masoero E, Manzano H, Del Gado E, Pellenq RJ-M, Ulm F-J, Yip S. Kinetic simulation of the logarithmic creep of cement. *Mechanics and Physics of Creep, Shrinkage, and Durability of Concrete: A Tribute to Zdeněk P Bazant: Proceedings of the Ninth International Conference on Creep, Shrinkage, and Durability Mechanics (CONCREEP-9)*, September 22-25, 2013 Cambridge, Massachusetts. 2013:166-73.
- [200] Del Gado E, Ioannidou K. Nanoscale numerical study of CSH precipitation and gelation. *Mechanics and Physics of Creep, Shrinkage, and Durability of Concrete: A Tribute to Zdeněk P Bazant: Proceedings of the Ninth International Conference on Creep, Shrinkage, and Durability Mechanics (CONCREEP-9)*, September 22-25, 2013 Cambridge, Massachusetts: ASCE Publications; 2013. p. 30.
- [201] Ioannidou K, Pellenq RJ-M, Del Gado E. Controlling local packing and growth in calcium–silicate–hydrate gels. *Soft matter*. 2014;10(8):1121-33.
- [202] Gonzalez-Teresa R, Dolado JS, Ayuela A, Gimel JC. Nanoscale texture development of C-S-H gel: A computational model for nucleation and growth. *Appl Phys Lett*. 2013;103(23).
- [203] Etzold MA, McDonald PJ, Routh AF. Growth of sheets in 3D confinements - a model for the C-S-H meso structure. *Cement and Concrete Research*. 2014;63:137-42.
- [204] Bentz DP. Three-Dimensional Computer Simulation of Portland Cement Hydration and Microstructure Development. *Journal of the American Ceramic Society*. 1997;80(1):3-21.
- [205] Haecker C-J, Garboczi EJ, Bullard JW, Bohn RB, Sun Z, Shah SP, Voigt T. Modeling the linear elastic properties of Portland cement paste. *Cement and Concrete Research*. 2005;35(10):1948-60.
- [206] Bittnar Z. Microstructure-based micromechanical prediction of elastic properties in hydrating cement paste. *Cement and concrete research*. 2006;36(9):1708-18.
- [207] Bishnoi S, Scrivener KL. μ ic: A new platform for modelling the hydration of cements. *Cement and Concrete Research*. 2009;39(4):266-74.