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Nano-engineering of construction materials using molecular dynamics simulations: Prospects and challenges

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ABSTRACT

In recent years, research articles involving molecular dynamics simulations of construction materials have grown significantly in number. The growth reflects an emerging need to understand microscopic physical and chemical processes, which are fundamental to further improve the macroscopic performance of construction materials. Nano-engineering, as a concept about manipulating material structures for creating new materials or modifying existing materials, highly depends on the understanding of materials at the nanoscale, where molecular dynamics simulation becomes an effective and powerful investigation tool. In this paper, the applications of molecular dynamics simulations in understanding the fundamental deformation mechanism of various construction materials including concrete and cement, fiber-reinforced polymers and related bonded systems upon nano-engineering approach are presented. In addition, the study on nature materials towards their structural morphology and functions at the atomistic level is illustrated so as to inspire the future development of advanced construction materials. The challenges and innovations associated with nano-engineering are also discussed.

1. Introduction

The breakthroughs in nano-engineering over the past few decades enable investigations upon intricate phenomena in material systems at the nanoscale, which contributes to the development of strengthened materials with unique features. As construction materials are closely related to our daily lives and people become more aware towards sustainability, their mechanical behaviors, especially durability, become the key concern. It has been reported that most of construction materials look good when only focusing on their performance in a short term, but they can significantly deform or even fail upon external loadings (which is within its designed capability) in natural environments over a certain period of time due to the deterioration within materials or the interaction between materials and surroundings [1–3]. The material deformations always originate from the atomistic scale, which are hardly noticeable using traditional techniques including existing experimental detection and continuum theory. Such an obstacle has hindered the advancement of construction materials in the past few decades until the nano-engineering concept (through simulations) has emerged as an effective approach, which can really break the ice for the research field of construction materials. In the past few years, such simulation approach has been developed significantly in response to the increasing demand for enhancing construction materials with satisfactory performances and delayed degradations. More importantly, the use of nano-engineering in the field of construction materials can help us discover various fundamental failure mechanisms inside material systems and such information provides lots of inspirations for structural design, which is beyond the scope of civil engineering.

The nano-engineering employs the perspective from the nanoscale towards in-depth understanding of underlying properties and deformation mechanisms that govern macroscopic performance of construction materials, and the procedure is implemented as shown in Fig. 1. The modeling scheme using molecular dynamics (MD) simulations for addressing nanostructures and atomistic interactions inside material systems is essential when applying the nano-engineering approach as it is required to evaluate atomistic movements based on material science and inherent behaviors of actual materials. MD simulations serve as effective computational experiments to characterize material properties and predict mechanical responses, which can be used to verify theoretical hypotheses. An earlier development of MD simulation was reported in 1950s for a study on the dynamics of a hard sphere system consisting of several hundreds of particles [4]. Since

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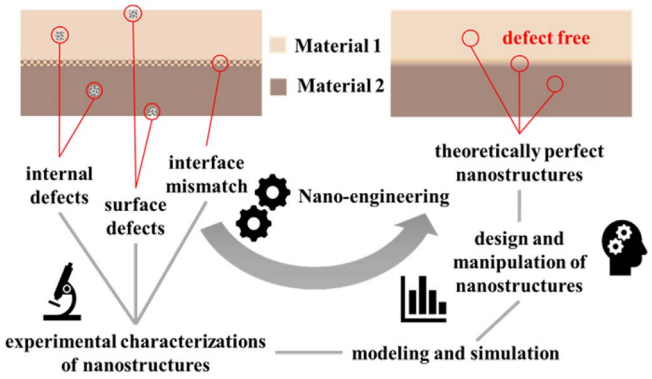

Fig. 1. Proposed implementation of nano-engineering processes for enhancing material properties.

then, the advancement of MD simulation has been observed with the evolution of computational power in the last few decades. MD simulation represents a powerful tool for potential applications in various research fields including physics, chemistry, biology, bio-engineering and medicine [5,6]. Recently, efforts have been made for applying the method to the fields of structural mechanics and civil engineering. Traditionally, the classical continuum mechanics theories have been the basis for most computational methods used in various engineering fields including civil and mechanical engineering; examples are finite element analysis, finite difference method, finite volume and boundary element methods. The capability of the continuum approach is limited when structural solution at a small length scale is of concern. In other words, the predictions about material behavior should be made from a fundamental bottom-up perspective.

In MD simulations, materials can be treated as aggregation of atoms which are regarded as classical (non-quantum and subjected to Newton's Laws of motion) mass particles. This method is based on trajectory of atoms in the modeling system and can provide data that involves time evolution of material nanostructures subjected to external conditions. Basically, the computation involves iterative manipulation of three important parameters including displacement/position, velocity and acceleration as the solution of Newton's second law. To improve the calculation efficiency in the iterative processing, different numerical methods have been developed, for example, Verlet integration, leapfrog integration, velocity Verlet integration and predictor-corrector integration [6]. These algorithms have their own strengths and weaknesses, and are feasible to be employed for different materials. The forcefield plays an important role in describing interatomic interactions, and the selection of forcefield critically determines the validity of MD simulations. A number of widely used forcefields have been introduced for different kinds of material systems [7–10]. These forcefields target for either inorganic or organic polymers, while no direct description for general construction materials is available. The common functional terms including general bonded and non-bonded energies from these forcefields have been adopted in construction materials as the formulation of interactions can be shared in similar structures. For the MD simulations without any chemical reaction, the non-reactive forcefields can be employed to describe the interactions between different components in the material systems. However, the connectivity among components can be altered in special conditions associated with release of atoms as well as generation of new phase (*i.e.* involving chemistry), where the non-reactive forcefields are no longer available. To simulate bond breaking and bond formation in material systems, the reactive forcefield such as ReaxFF [10] can be used. The reactive MD enables the investigations of chemical reaction mechanisms including catalysis, pyrolysis and combustion. The enrichment of forcefields for various interactions satisfies the need of describing the interactions between dissimilar components as well as between materials and external surroundings such as water or other molecules in solvent environments, which cause the structural change in construction materials and affect material properties in a long run. The results generated from MD simulations can provide the key missing knowledge of traditional construction materials at molecular level, which has been usually overlooked for the past few decades.

When applying MD simulations in construction materials research, there are critical challenges covering how to extract information during physical and chemical processes from the nanoscale and to relate the nanoscale information to the macroscopic material performance. Although MD simulations have been widely applied on the study of construction materials over the past few years, this computational approach has a limitation in both the time scale and the length scale. In view of such a small magnitude of time and length scale, which are generally nanosecond (10^{-9} s) and nanometer (10^{-9} m), MD simulations are not suitable for directly studying construction materials as they are always large in length scale and their performance in a long run is always the key for a sustainable design. To resolve the limitation in both the length scale and the time scale, the multiscale modeling for construction materials is proposed that can link MD results to microscopic observations so as to interpret material behaviors. Recent advances in computational power and algorithms have increased the timescales for capturing material behaviors over millisecond-scale. These limitations further motivate the development of applying nano-engineering concept in construction materials.

In this paper, the nano-engineering approach using MD simulations on the studies of construction materials, as well as the recent progress on the fundamental understanding of construction materials and their behaviors, is reviewed with an emphasis on the linkage between the nanoscale and the macroscale, and the transition from research to practical applications. Widely used construction materials like concrete, fiber reinforced polymer (FRP) and their related bonded structures are selected as representative material systems here. For the selected material systems, atomistic modeling, forcefield selection and simulation details under different conditions are introduced and evaluated. MD simulations demonstrating how physical and chemical processes behind macroscopic material performance are presented. In addition, the state-of-the-art related to bio-inspired materials provides a new insight towards the future research direction for construction materials. It is envisioned that the development of construction materials should be founded on the active learning from the natural features of biomaterials. The crucial challenges of nano-engineering approach using MD simulations are also addressed, which are important for our future research and development. This review demonstrates the capability of nano-engineering for research of construction materials, which is a breakthrough from the traditional idea which normally sticks to the investigations of construction materials using macroscale models only to an innovative approach which integrates two extreme and disconnected fields (*i.e.* discrete versus continuum) as a whole. The comprehensive knowledge of the existing research findings and the clear understanding upon the limitations can accelerate the progress of nano-engineering for construction materials.

2. Concrete and cement

As a complex composite, concrete consists of a binding phase (cement matrix) and a particulate phase (aggregates). In normal strength concrete, the particulate phase is much stronger than the binding phase. Therefore, mechanical properties of concrete largely depend on the cement matrix. In this composite material system, the cement matrix is the key focus of MD simulations, which contains four major components as shown in Fig. 2. All of these components react with water to generate hydration products. Nanostructures, hydration processes and mechanical properties of the unhydrated clinkers as well as hydration products are of major interests. Besides the analysis of material structure and basic mechanical properties, the nano-engineering approach is particular useful to facilitate the study of time-dependent behavior and decode the nanogranular origin of creep in concrete [11].