Evolving the C-S-H Packing Density at the Microscale

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PROBLEM

Cement paste is a complex multiphase material, roughly 50 percent of which, by volume, is composed of calcium-silicate-hydrates (C-S-H). The C-S-H phase, which lends the material its rigidity, appears to be a dispersion of nanometer-sized particles that densify during the course of the hydration reaction (Ioannidou *et al.,* PNAS 2016). Because the mechanical properties, early-age internal stresses, and microstructure are critically dependent on the distribution of the high density (HD) and low density (LD) C-S-H product, research efforts are underway to better understand nanoparticle packing density at the scale of hundreds of micrometers, where a binary mixture of clinker grains and saturated pore space evolve into a porous hydrated gel. This research brief displays simulated snapshots of cement paste at varying hydration degrees and predicts the evolution of the HD and LD peaks for the distribution of the indentation modulus also observed in nanoindentation experiments.

APPROACH

Phase-field modeling has been used in material science to describe the microstructural evolution of materials such as undercooled metals, lithium intercalation in batteries, and hydrate formation in subsurface geological systems. Though the technique can accurately simulate nucleation (the first process that occurs in the formation of a solid from a solution, liquid, or vapor) and growth processes, it has thus far not been widely applied to cement-based materials. To adopt phase-field modeling for cement solidification, researchers have derived a function for the free energy of the cement system that depends on a select set of field variables that are relevant in describing its local mechanical properties. One of these variables is the C-S-H packing density – the volume fraction occupied by the C-S-H nanoparticles – which has been shown to predict the local elasticity and toughness of cement paste.

Traditional numerical models have sharp interfaces between solid and pore space. Phase-field models introduce diffuse interfacial regions (allowing the packing density to vary smoothly throughout the cement domain) that localize the reaction kinetics (see Fig. 2, page 2). By modeling the nucleation and growth of the solid products, we can better understand how local stiffening of the paste influences its mechanical performance.

FINDINGS

The panel in Fig. 2 provides snapshots of the packing density, and modulus in time. Heterogeneous nucleation causes growth of cement products as a shell around the anhydrous source particles, while homogeneous nucleation sites allow C-S-H to precipitate in the open pore space. Similarly, the HD signature initiates around the source particles and moves to occupy regions formerly occupied by the clinker grains, while the LD signature arises in the intergranular regions. Fig. 1) displays the evolution of the means and standard deviations of the elastic modulus for the LD and HD signatures as the reaction progresses. Here, our model predicts an initial rapid gain in stiffness until the two peaks start to converge at later stages in the reaction; these are trends that have been verified experimentally.

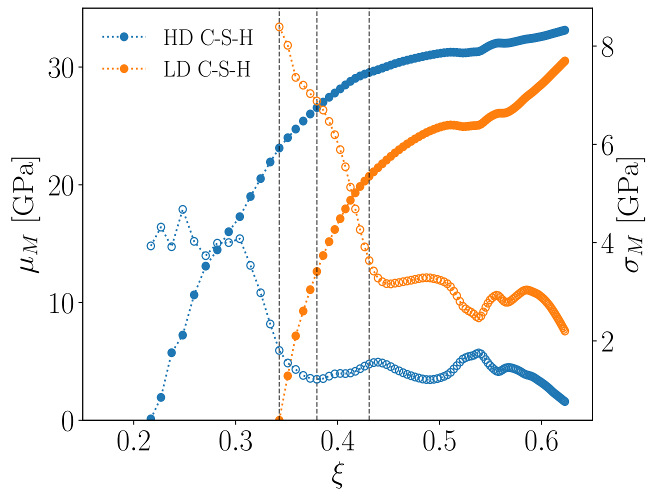

Fig. 1) Plot of the means of the LD C-S-H and HD C-S-H signatures in function of the degree of hydration as predicted from our phase-field model (closed circles refer to the means μ_M of the bimodal distribution, open circles refer to the standard deviations, σ_M; see bottom panel in Fig. 2 for distributions).

WHY DOES THIS RESEARCH MATTER?

- This research brief introduces a novel approach to simulate the micromechanical evolution of the LD and HD C-S-H signatures in cement paste.
- The phase-field approach allows us to understand the interaction between cement paste solidification, development of eigenstresses (*e.g.*, early-age volume changes), and externally supplied loads.
- The work provides a tool to upscale mechanical information gleaned from nanoscale experiments and simulations.

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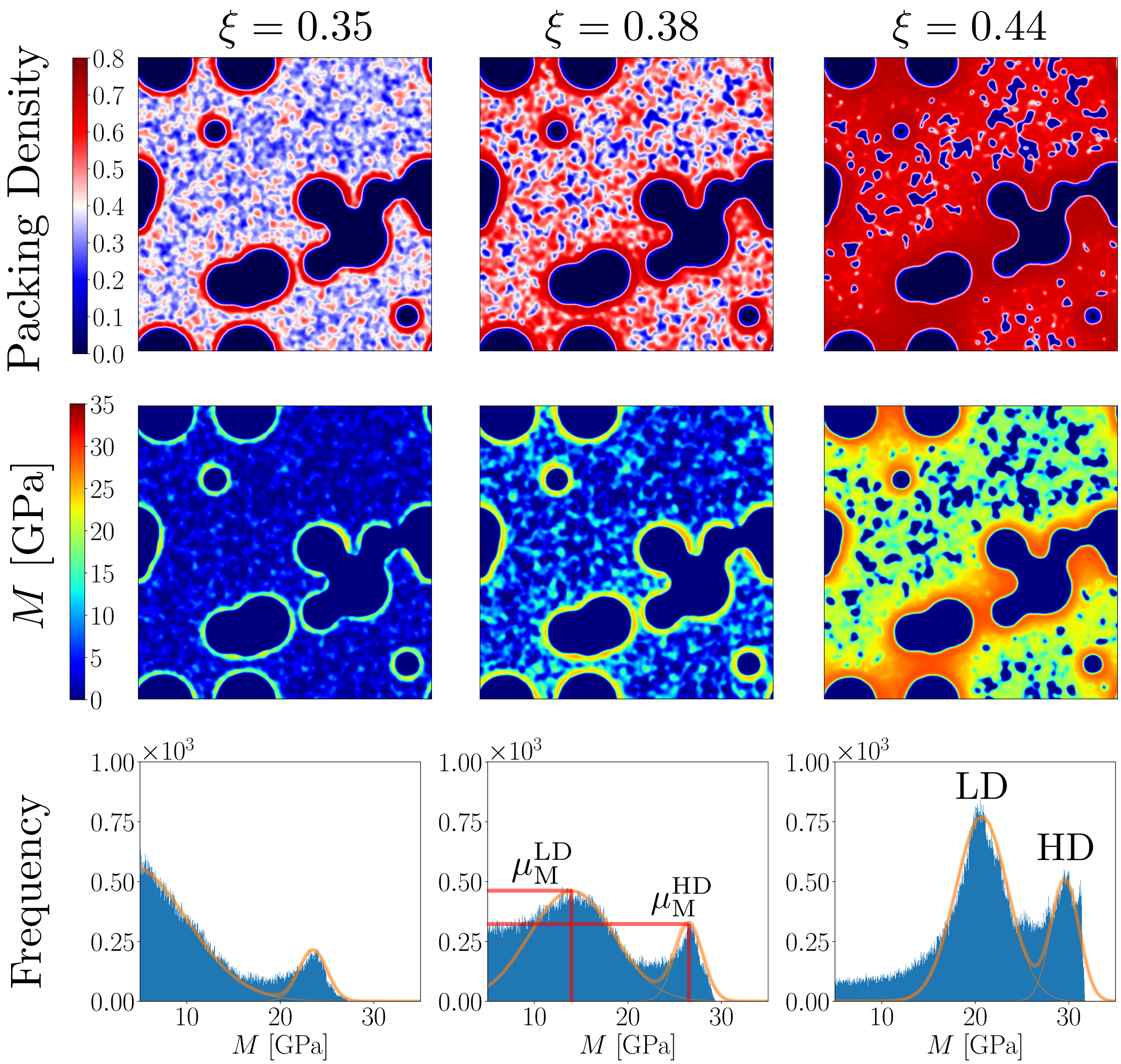

Fig. 2) Snapshots in time of the C-S-H packing density (top), the local value of the indentation modulus (middle), and the frequency distribution of the modulus (bottom), as predicted using a phase-field model. The degree of hydration ξ for each column is indicated at the top.