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Applying Tools from Glass Science to Study Calcium-Silicate-Hydrates

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Abstract:

To explain the similarities between a glass and amorphous C-S-H, a C-S-H molecular structure with stoichiometry of $(\text{CaO})_{1.7}(\text{SiO}_2)_1(\text{H}_2\text{O})_{1.9}$ is produced using a mixed reactive-nonreactive force field modeling. As the consequence of reactive modeling using REAXFF potential, part of water molecules in the interlayer spacing dissociate in to hydroxyl groups and proton, which produces Ca-OH bonds. In addition, it is shown that monomers condensate to produce dimmers. This reduces the monomer content and increases the mean silicate chain length. Comprehensive topological analysis is performed to identify the local environment of each atom, which is indicative of short range order in C-S-H. Specially, the topological analysis is shown to be essential to distinguish between oxygen atoms in water, hydroxyl groups, silica chain and calcium oxide sheets. The medium range order in C-S-H is shown to exist using first sharp diffraction pattern derived from structure factor calculations.

Introduction:

The main hydration phase of cementitious systems is calcium-silicate-hydrate (C-S-H). This phase is the binding phase responsible for concrete's strength, durability, viscoelastic and creep properties. Since all the physical properties of C-S-H originate from the nano-scale, a special attention is drawn to the molecular structure of C-S-H in the past few years. Specially, (Pellenq et al. 2009) proposed a realistic C-S-H model which exhibited many features of C-S-H nanostructure. Using the tools in statistical physics, the realistic C-S-H model were further analyzed in more details (Abdolhosseini Qomi et al. 2012; Ji et al. 2012; Youssef et al. 2011). Recently, the realistic C-S-H was further developed to include Ca-OH bonds (Manzano et al. 2012). This updated model confirmed again that realistic C-S-H models could reproduce both density and mechanical properties of C-S-H structures. The common point between all C-S-H structures are that they are composed of quasi-octahedral calcium-oxide layers with defective silica chains on the either sides. The calcium-silicate lamellar layer is negatively charged which is charge-balanced with Ca^{2+} cations in the interlayer spacing. The interlayer spacing separates stacks of calcium-silicate sheets.

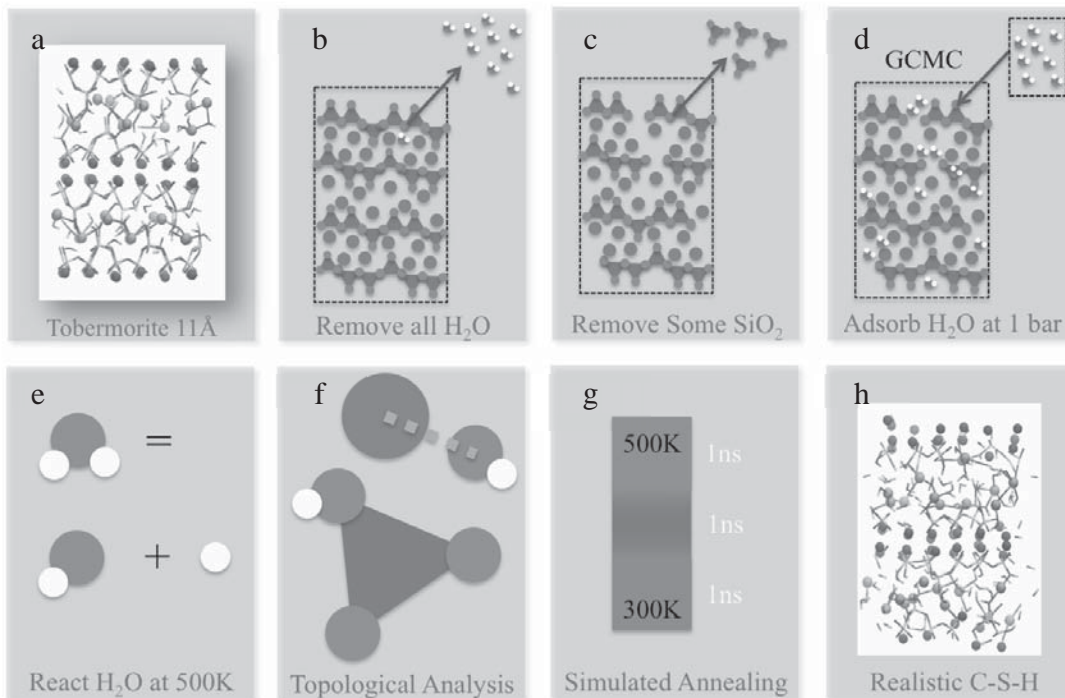


Figure 1: Different stages for the preparation of a realistic C-S-H model. a) Starting from a super-cell of Tobermorite 11Å. b) Removing water molecules from the structure. c) Removing SiO₂ bonds from the calcium-silicate backbone. d) Adsorbing water in the interlayer and defect sites. e) Reactive force field modeling at elevated temperature. f) Topological analysis to identify local environments. g) Simulated annealing using non-reactive potential. h) A snapshot of a realistic C-S-H model.

The molecular structures of C-S-H and glasses have many features in common. Given the recent advances in glass physics, it is of the general cement and concrete community to explore the molecular structure of C-S-H in terms of a glass. There are several prevalent tools such as topological analysis, first sharp diffraction patterns and constraint theory that can already be applied to the molecular structure of C-S-H. Using the tools in statistical physics, a C-S-H sample is created with Ca/Si=1.7. The topological analysis is performed to identify the short-range order in the system. The medium range order is analyzed afterward to demonstrate that the order extends beyond the first coordination shell of atoms.

Realistic Modeling of C-S-H at Nano-Scale:

The methodology to produce a realistic C-S-H molecular structure is a combination of several atomistic-scale classical simulation techniques at different stages of the model preparation (see figure 1). The main statistical mechanics techniques employed are internal energy relaxation at constant volume or pressure, Grand Canonical Monte Carlo (GCMC) for water adsorption, NPT and NVT molecular dynamics using both reactive and non-reactive potentials at room and elevated temperatures. The interatomic interactions are described via REAXFF (Manzano, Pellenq, et al. 2012), CSHFF potential (Shahsavari et al. 2011) and a modified version of CSHFF potential to include the interactions with hydroxyl groups. The original CSHFF interatomic potential is a point-charge model designed to reproduce C-S-H's mechanical

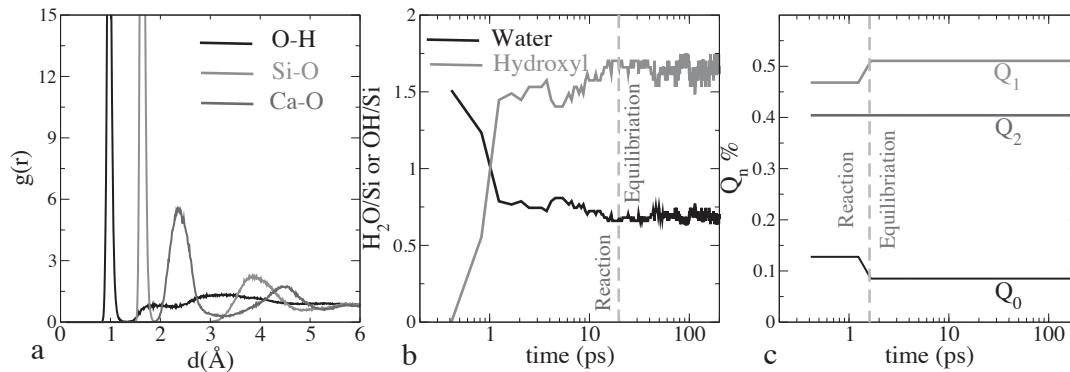


Figure 2: Reactive force field modeling in canonical ensemble. a) Radial distribution function for Si-O, Ca-O and O-H bonds. b) Dissociation of water molecules in C-S-H and production of hydroxyl groups. c) Condensation of silica groups in the silicate chain.

properties. The CSHFF potential has the ($E_{CSHFF}=E_{Coulomb}+E_{LJ}+E_{Radial}+E_{Angular}$) form. $E_{Coulomb}$, E_{LJ} , E_{Radial} , and $E_{Angular}$ are the electrostatic, short-range Van der Waals in the form of Lennard-Jones potential, bond stretching and bond bending contributions to the potential energy of the ionic-covalent system. CSHFF is seen as an improved version of the generic ClayFF potential (Cygan et al. 2004). Despite all the advantages of using CSHFF potential, this force field is unable to describe chemical reactions.

REAXFF potential was subsequently developed and applied to C-S-H to study the state of water in the C-S-H's nano-porous medium (Manzano et al. 2012). REAXFF is a reactive force field originally based on the same ideas as bond order potentials (Tersoff 1988) with polarizable charge model. In this force field, the total potential energy reads ($E_{REAXFF}=E_{Coulomb}+E_{VdW}+E_{Radial}+E_{Angular}+E_{lp}+E_{OverCoord}+E_{UnderCoord}$). E_{lp} is lone pair energy, $E_{OverCoord}$ and $E_{UnderCoord}$ are over- and under-coordinated energy contributions, respectively. These three terms are added to this potential to make appropriately capture chemical reactions. REAXFF shows the ability to define each individual interaction between atoms depending on their environment. For more detailed discussion on the REAXFF potential, interested readers are referred to the work of (Russo Jr. and van Duin 2011).

To build a C-S-H model with $Ca/Si=1.7$, we started from a periodic simulation box containing $2*3*1$ unit cells of Hamid's structure of 11\AA Tobermorite (Hamid 1981). At this stage, we considered an anhydrous version of this structure, as we were only interested in creating the model itself. To produce the calcium-silicate backbone of the sample, a simple computer program was written that uses a random number generator to remove some SiO_2 groups with the constraint producing as much dimers, pentamers and octamers as possible. Since SiO_2 is a neutral group, the electro-neutrality is maintained. In fact, upon removal of all the bridging silica sites from the initial crystalline structure, the Ca/Si ratio is found to be 1.5. Therefore, some monomers inevitably exist in the initial solid skeleton of C-S-H samples.

We used the Grand Canonical Monte-Carlo (GCMC) simulation technique to adsorb water in the interlayer spacing and defect locations. GCMC is at constant volume V in contact with infinite fictitious reservoir of particles with chemical potential, μ , at temperature T . We did not calculate the entire water adsorption/desorption isotherm

but perform a single GCMC simulation with the water chemical potential fixed to a value that corresponds to the bulk liquid phase with a density of 1 gr/cm^3 at room temperature ($\mu=0 \text{ eV}$ for the used flexible SPC water potential model). All the GCMC calculations are performed via GULP (Gale 1997).

All reactive simulations are performed using LAMMPS (Plimpton 1995), using velocity Verlet time integration scheme. In order to appropriately describe chemical reactions, the time step is set to 0.1fs. Additionally, to trigger and facilitate the reaction of water molecules, REAXFF simulations are carried out at 500K. This helps the water molecules to overcome the reaction energy barriers. Initially, all samples are relaxed in canonical ensemble (NVT) for at 200ps using Nose-Hoover thermostat. After relaxation in NVT ensemble, the samples are further relaxed in isothermal-isobaric ensemble (NPT) at the 500K and 1atm. The overall performance of a C-S-H sample with $\text{Ca/Si} = 1.7$ is presented in Figure 2.

Figure 2.a provides the radial distribution function, RDF or $g(r)$, of Si-O, Ca-O and O-H bonds. Since the peaks in $g(r)$ are intact, the slight elevated temperature has not affected the solid backbone of the C-S-H. It should be also noted that while Si-O and O-H RDFs have a very defined first sharp peaks, the Ca-O RDF exhibits a wider first peak. Ca-O bond has a much larger radial excursion meaning that Ca-O bond is not as stiff as Si-O and O-H. As it can be seen in figure 2.b, in the very first few picoseconds of the simulation, a large portion of water molecules dissociates to form OH^- and H^+ ionic pairs. While the hydroxyl groups coordinate with Ca^{2+} ions, the produced protons reacts with non-bridging oxygen atoms in silicate groups. No hydrogen atom was found coordinated to the bridging oxygen shared between adjacent silicate groups. The dissociation mechanism affects the large portion of interlayer water molecules in the C-S-H and the dissociation percentage depends on the Ca/Si ratio which is directly proportional to the number of non-bridging oxygen atoms in silicate chain. Reactive modeling also affects the solid skeleton of C-S-H. Figure 2.c shows the effect of reactivity on condensation of silicate groups. It is observed that silicate groups condensated in this C-S-H model. In the particular case, a pair of monomers has condensate to form a dimer. This is in agreement with DFT calculation of isolated silicate groups (Manzano et al. 2011) showing that dimers have high stability index. The observed condensation mechanism is triggered by two silicate tetrahedra pairing in which a dimer is produced and an oxygen atom is released in the process. The free oxygen pairs with a H^+ atom and to complete the reaction path, the product hydroxyl group coordinates with Ca^{2+} atoms in the interlayer spacing. This signifies that due to random "cutting" of chains, some monomers have extremely unrealistic configuration. This unrealistic state is relaxed via polymerization of monomers producing energetically more stable dimers.

Topological Analysis:

REAXFF modeling is computationally expensive to undertake. In order to overcome the prohibiting computational cost of reactive modeling in extensive mechanical testing required to be performed on all of the C-S-H samples, all the samples are transferred to non-reactive modified C-S-H-FF environment after reaction. As the direct consequence of reactive modeling, the local environment of atoms undergoes drastic changes. This adds a level of complication and necessitates a precise

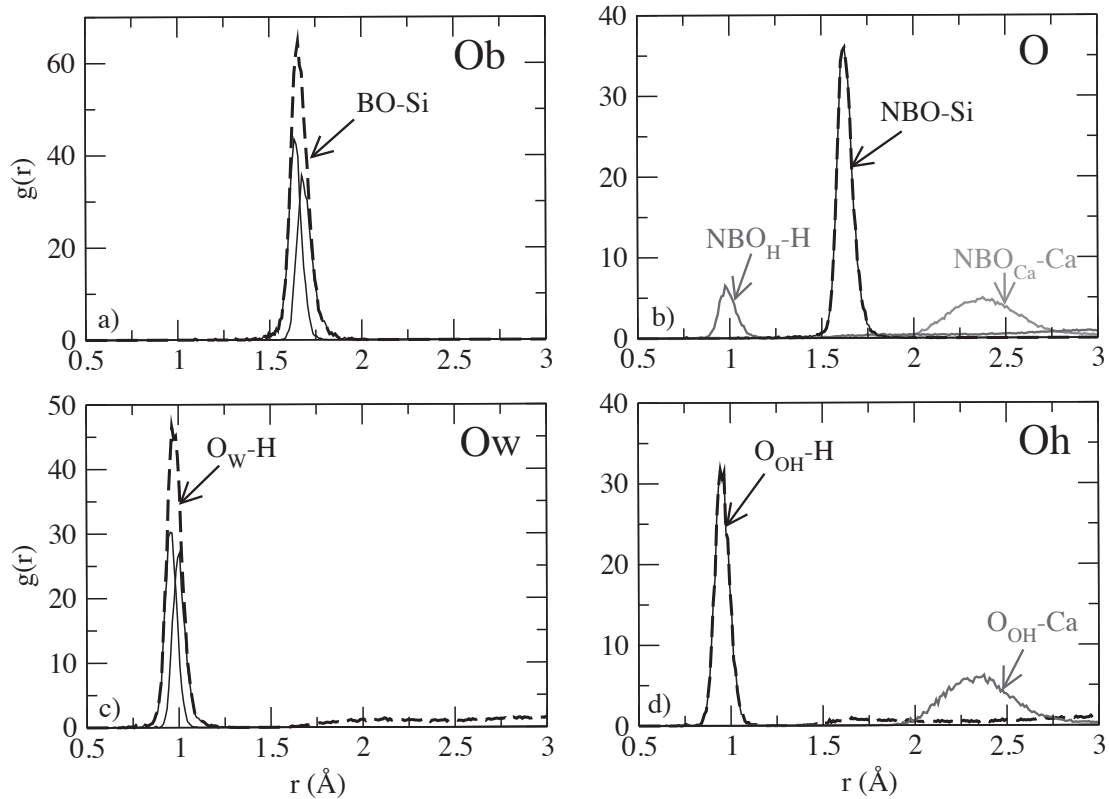


Figure 3: Radial distribution functions of Si, Ca, and H cations around Ob (a), O (b), Ow (c) and Oh (d). Figures a) and b) show the contributions of the two nearest Si neighbors and figures c) and d) the contributions of the two nearest H neighbors.

characterization of local environment of each single atom. Such a precise analysis can be performed using the fundamental ideas in topological constraint analysis (Bauchy and Micoulaut 2013). In C-S-H's molecular structure, Si, Ca and H cations are always connected to O atoms, the latter showing different local environment (see Figure 3). In order to differentiate these species, we performed a careful topological analysis of the coordination of each O atom. Bridging oxygen atoms (Ob) are thus defined as oxygen atoms showing exactly two Si neighbors in their O-Si first coordination shell (FCS), which limit has been fixed as the first minimum of the $g_{\text{Si-O}}$, typically 2.5\AA . On the contrary, non-bridging oxygen atoms (O) show only one Si in their O-Si FCS. Those species arise from the depolymerization of the silicate network by Ca and H cations and can belong to hydroxyl groups O-H (Oh) if they show an H neighbor in their O-H FCS (minimum of the $g_{\text{O-H}}$ RDF, typically 1.3\AA) or be connected to Ca atoms otherwise. Remaining O atoms that are not part of the silicate network have then been respectively differentiated into water oxygen atoms (Ow) and hydroxyl group oxygen atoms (Oh) when they respectively show two and one hydrogen atom in their O-H FCS. Following the topological analysis, the sample was relaxed for 1ns at 500k using modified C-S-H-FF potential in isobaric-isothermal ensemble with time steps as large as 1fs. All samples are subsequently quenched over 1ns to 300K and further relaxed in NPT ensemble for another 1ns at 300K to make sure that all the macroscopic observables have relaxed and converged to a proper value.

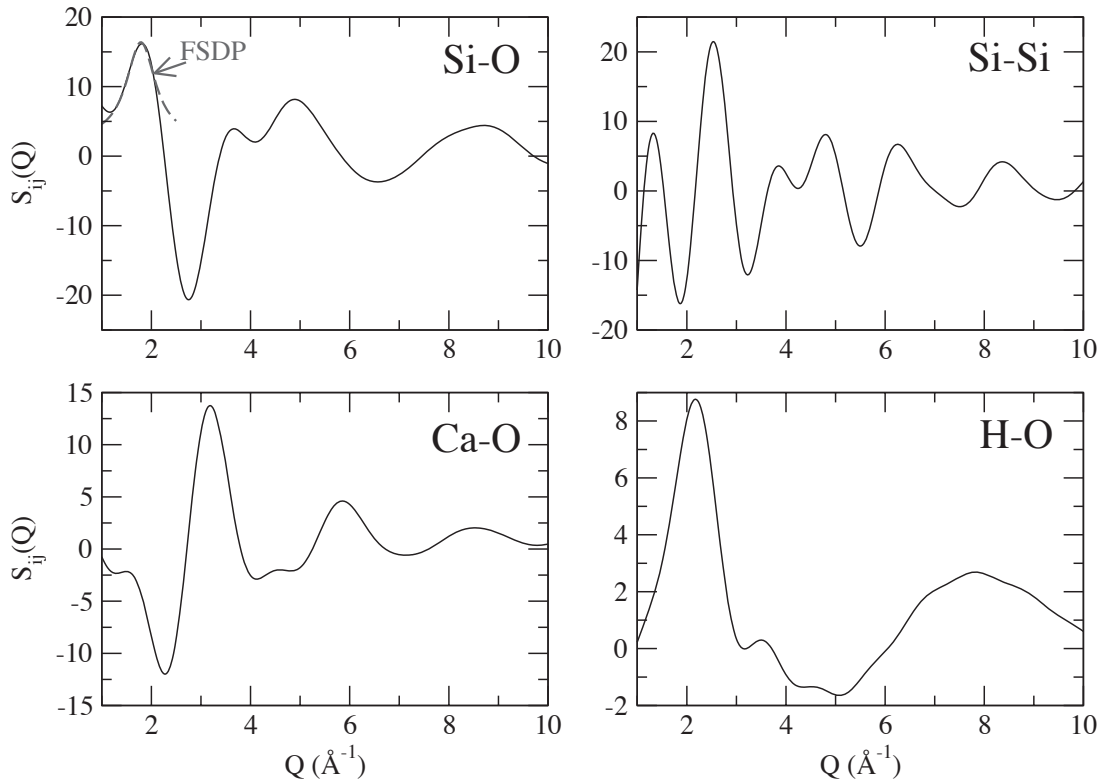


Figure 4: Computed a, Si-O, b, Si-Si, c, Ca-O and d, H-O structure factors at Ca/Si=1.7. The blue broken line shows a fit of the first sharp diffraction peak with a Lorentzian function.

Medium Range Order:

As presented before, RDFs give insights into the short-range order of the structure of the material, this length scale being mostly driven by coordination numbers and bond lengths. We analyzed the medium range order to understand the extent of order in C-S-H. To do so, we largely relied on tools introduced in glass science. The medium range order can be captured by the partial structure factors, which can be computed from the RDFs $g_{ij}(r)$:

$$S_{ij} = 1 + \rho_0 \int_0^R 4\pi r^2 (g_{ij} - 1) \frac{\sin(Qr)}{Qr} F_L(r) dr$$

where $Q = 2\pi/r$ is the scattering vector, ρ_0 is the average atom number density and R is the maximum value of the integration in real space (here $R = 6\text{\AA}$). The $\frac{\sin(\frac{\pi r}{R})}{(\frac{\pi r}{R})}$ term is a Lorch-type window function used to reduce the effect of the finite cutoff of r in the integration (Wright 1988). The use of this function reduces the ripples at low Q but can induce a broadening of the structure factor peaks. Figure 4 shows Si-O, Si-Si, Ca-O and H-O partial structure factors at Ca/Si=1.7, which are by all means similar to typical structure factors observed in silicate glasses.

Among the different features of structure factors, the so-called first sharp diffraction peak (FSDP) has received a lot of attention in glass science. Starting from the

principal peak, which position $Q_p = 2\pi/r_p$ is associated to the nearest-neighbor distance r_p , the FSDP is defined as the next peak located a lower $Q < Q_p$. It is thus related to the structural correlations in the medium range order at $r > r_p$. This feature has been observed both in covalent (Elliott 1991; Wilson and Madden 1994) and ionic (Wilson and Madden 1994) amorphous system. The FSDP origin is now usually explained by using a void-based model (Uhlherr and Elliott 1994; Zaug et al. 2008) in which ordering of interstitial voids occurs in the structure.

The FSDPs we obtained from simulations were further studied by fitting them with Lorentzian functions (example of fitted function can be seen on Figure 4). This choice is supported by the fact that the experimental results in neutron scattering factor of silica can be better fitted with a Lorentzian function than with a Gaussian one (Wright et al. 1991). It should be noted that the fit has been done on the low Q part of the FSDP to avoid the contribution of the following peaks. This allows us to track precisely the FSDP peak intensity, position and full-width at half maximum (FWHM) for each sample. Coming back to the real space structural correlations, the FSDP peak position Q_{FSDP} is usually related to a characteristic repetition distance $d = 2\pi/Q_{FSDP}$. The effect depolymerization of the network (a decrease of the atomic order) is associated to a decrease of the intensity of the FSDP and a decrease in the characteristic distance d (Bauchy 2012).

Conclusion:

In this paper, a C-S-H molecular structure with stoichiometry of $(\text{CaO})_{1.7}(\text{SiO}_2)_1(\text{H}_2\text{O})_{1.9}$ was produced using a mixed reactive-nonreactive force field modeling. Using REAXFF potential, part of water molecules in the interlayer spacing dissociates in to hydroxyl groups and proton. It was also shown that monomers condensate to produce dimmers. This reduces the monomer content and increases the mean silicate chain length. Comprehensive topological analysis is performed to identify the local environment of each atom, which is indicative of short-range order in C-S-H. Specially, the topological analysis is shown to be essential to distinguish between oxygen atoms in water, hydroxyl groups, silica chain and calcium oxide sheets. The medium range order in C-S-H is shown to exist using first sharp diffraction pattern derived from structure factor calculations.

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