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Quantifying the Processes at the Origin of the Dielectric Response of Cement-Based Materials with Molecular Dynamics Simulations

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Abstract—The pore phase determines the dielectric and electrical responses of cement-based materials. Porosity is hierarchical in these materials with pore classes including macro, capillary, and nanopores. This work shows how molecular dynamics simulations provide quantitative information about the complex dielectric and electrical response for free water and ions, surface water and physically bound ions species, water and ions confined in nanopores, and also OH groups in the pore wall.

Index Terms—Molecular dynamics, susceptibility, electrical conductivity, cement-based materials

I. INTRODUCTION

Electromagnetic measurements, including dielectric permittivity and electrical resistivity, are among the main methods for non-destructive evaluation and testing of concrete structures. The interpretation of these measurements relies on comprehending the contributions of the various phases present in cement-based materials, which are heterogeneous multi-phase materials with hierarchical porosity.

Pore sizes in cement-based materials span several orders of magnitude: from macroscopic air voids to capillary pores and nanopores. Nanopores include calcium silicate hydrates (C-S-H) gel pores and interlayer pores. Water and ions in these different pore classes, especially in the smaller pores, are expected to exhibit distinct behavior compared to the bulk (e.g. [?], [?], [1]). Molecular simulations arise as valuable tools for quantifying relaxation processes in systems at the nanoscale based on fundamental physical principles. These simulations have been used to obtain electromagnetic properties of bulk multi-component aqueous solutions and confined systems [2]. They can also provide a fundamental understanding of the relaxation processes occurring due to fluid-solid interactions at the nanoscale.

Here, we demonstrate how molecular dynamics simulations provide information on the complex frequency-dependent dielectric and electrical response in large pores, close to the pore surface and under nanopore confinement in cement systems. Additionally, we discuss how these simulations can be employed to acquire information about relaxation processes at low frequencies.

II. FREQUENCY-DEPENDENT DIELECTRIC RESPONSE AND ELECTRICAL CONDUCTIVITY FROM MOLECULAR SIMULATIONS

The dielectric permittivity ϵ is computed in a molecular simulation from the Fourier transform of the auto-correlation of equilibrium polarization fluctuations [3]:

$$\epsilon(f) = 1 - \frac{1}{3Vk_B T \epsilon_0} \int_0^\infty e^{-2\pi i f t} \langle \vec{P}(0) \cdot \dot{\vec{P}}(t) \rangle dt \quad (1)$$

where $\vec{P}(t) = \sum_{i=1}^n q_i \vec{r}_i(t)$ is the total polarization calculated for a system with n particles i with charge q_i ; $\dot{\vec{P}}(t)$ is the time-derivative of the total polarization; V and T are the volume and temperature, respectively; and k_B is the Boltzmann constant.

In porous materials with aqueous ionic pore solution, the total polarization is the sum of the contributions of the water \vec{P}_W , ionic \vec{P}_I , and solid \vec{P}_S polarizations: $\vec{P} = \vec{P}_W + \vec{P}_I + \vec{P}_S$.

The frequency-dependent ionic conductivity can be computed using the cross-correlations [4]:

$$\sigma(f) = \frac{1}{3Vk_B T} \int_0^\infty e^{-2\pi i f t} \langle \vec{J}_I(0) \cdot \dot{\vec{P}}(t) \rangle dt \quad (2)$$

where the ionic current is given by $\vec{J}_I(t) = \dot{\vec{P}}_I(t)$.

At the molecular level, the following contributions to electrical conductivity and dielectric permittivity can be identified:

- *water and ions in bulk portions of the pores (or free water and ions)*. The major part of the pore solution in capillary and macro pores is distant enough from the pore surface; thus, it can be considered as a bulk electrolyte. Bulk aqueous solutions mimicking the pore solutions in cement-based materials are created following the experimental composition [5]–[7].
- *Surface water and ions (or physically bound species)*. The species near the pore surface are directly affected by interaction with the solid walls. Hydrophilic surfaces possess adsorbed water layers with structures differing from bulk water [8]. Charged surfaces favor ion adsorption with electrical double layers formation. In C-S-H, surface

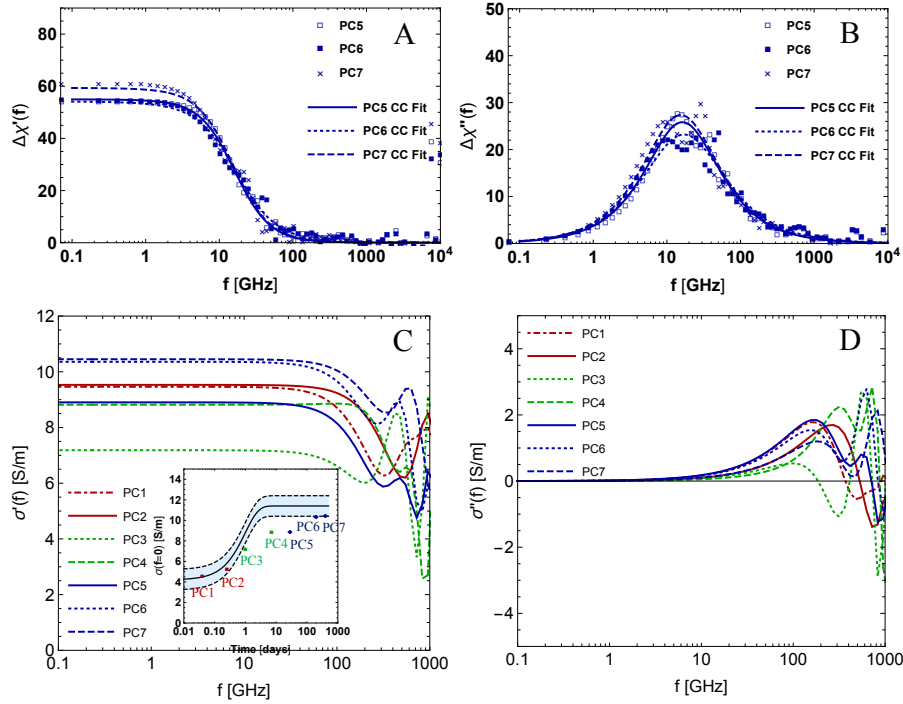


Fig. 1. Real (left) and imaginary (right) parts of the dielectric spectra (top) and conductivity spectra (bottom) of the pore solutions PC1-PC7.

water and ions show distinct structures and properties up to the fourth to fifth water layers (i.e., up to a distance of 7 to 10 Å from the surface) [9].

- *Confined water and ions.* When the pore thickness is on the order of the fluid particle size (i.e., in micropores and small mesopores), the effects of the two opposing surfaces might superpose, and the bulk zone of the pore disappears.
- *OH-groups in solids (or chemically bound water).* In hydrated minerals formation, water might react with the originating solid surface forming OH groups making part of the pore wall.

The C-S-H model proposed in ref. [10] is adopted. Parameters of ClayFF combined with SPC/E water are used. Molecular dynamics simulations are performed with LAMMPS.

III. RESULTS

Figure 1 shows the real and imaginary parts of the susceptibility and conductivity spectra of the bulk pore solutions PC1-PC7 (with PC1, PC2 concerning very early-age pore solutions; PC3 and PC4 early-age, and PC5-PC7 late ages). The age-dependent composition of the pore solutions is reflected in the dielectric spectra. Regarding static susceptibility, the difference between the maximum (PC3) and minimum (PC6) is approximately 20. This result shows that accounting for the composition variability of the pore is crucial to obtain the precise dielectric response of cement-based materials. The results regarding confined water in C-S-H nanopores are discussed in detail in ref. [2].

IV. CONCLUSIONS

Molecular dynamics simulations provide a powerful tool to compute the dielectric response of cement-based materials. The frequency-dependent response of the water and ions in bulk portions of the pores was quantifying, accounting for the complex, age-dependent composition of pore solution in cement systems. These results are valuable input for multiscale modeling of the dielectric response of cement-based materials. They can be used to improve the interpretation of dielectric measurements of cement-based materials. Work on the surface species, heterogeneity across pore thickness, and the contribution of OH groups in the pore surface will contribute to a better understanding of the dielectric response of cement-based materials.

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