Interactions between crystalline calcium silicate hydrates: grand canonical simulation of pressure and temperature effects

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INTERACTIONS BETWEEN CRYSTALLINE CALCIUM SILICATE HYDRATES: GRAND CANONICAL SIMULATION OF PRESSURE AND TEMPERATURE EFFECTS

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Abstract
The interactions between calcium silicate hydrates and pore solution at the nanoscale are crucial in physical phenomena related to the thermo-hydro-mechanical behaviour of cement-based materials. In this paper, these interactions are studied using grand canonical Monte Carlo simulations according to various temperatures and pressures. A nanocrystalline structure of calcium silicate hydrate (tobermorite) is considered. Micro-instabilities of snap-through type are identified. The corresponding potential of mean force, accounting for the interactions of the solid layers in drained conditions, is provided, which leaves rooms to upscale the behaviour of calcium silicate hydrates to the mesoscale.

1. Introduction

Adsorption related phenomena is reported to be at the heart of important features of cement-based materials behaviour such as drying shrinkage and hysteresis [1], creep [2], thermal expansion [3] and transmission of stresses between solid and liquids phases [4]. Adsorption takes place at the molecular scale and is recognized to be pressure and temperature dependent. The main product of cement hydration processes is calcium silicate hydrates, a microporous adsorbing material. Cement-based materials are generally subjected to variations of temperatures during their service life. Under temperature rise, fluid molecules are expected to desorb whereas the entire system is expected to show thermal expansion.

Simulations at the molecular scale are well suited to investigate adsorption phenomena in details. These simulations allow assessing water structuration as a function of confinement and the presence of ions in microporous materials [5]. Such approach have been use to

evaluate the intermolecular forces between solids layers of calcium silicate hydrates in drained conditions [6, 7]. Even if a macroscopically a nanoporous material, as calcium silicate hydrates, is not under drained conditions, at the nanoscale, due to the exchange of fluids between interlayer pores and gel pores the former class of pores can be seen as in drained conditions with respect to the fluid reservoir in gel pores. Experimental evidence [8] showing instantaneous changes in water population in these pores under temperature change corroborates this assumption regarding the internal migration of water. In this context, the thermodynamic ensemble adapted to study adsorption phenomenon is the grand canonical ensemble for the fluid combined with canonical ensemble for the solid layers: the total volume V and temperature T are fixed (while the total pressure P and entropy fluctuate), the chemical potential of the fluid μ_w is fixed (while the number of fluid molecules N_w fluctuates) and the number of atoms in the solid as well as counterions are fixed. This ensemble minimises the mixed thermodynamic potential $\Lambda(V, T, \mu_w)$. For a layered materials, the confinement pressure (in the direction orthogonal to the basal plane) $P = -\frac{\partial \lambda}{\partial d}\Big|_{T,\mu_w}$ can de defined in terms of Λ per unit area $\lambda(d, T, \mu_w) \equiv \Lambda(V, T, \mu_w)/A$, where d is the basal spacing. The energy profile for a system controlled by the volume is $\lambda = \lambda_0(d_0, T, \mu_w) - \int_{d_0}^{d} P \, d(d)$. The convex hull of λ, resulting from the integration of λ over a Representative Volume Element (RVE) represents the energy associated with all stable states of stacks under displacement control. The corresponding energy profile for a system controlled by the confining pressure is the Legendre transform of λ:

$$\lambda^* = \lambda + P \, d = \Lambda^*(P, T, \mu_w)/A \qquad (2)$$

This is what is called the free energy of swelling in clay science [5, 9]. This energy profile informs on the prevalence and stability of specific basal spacings.

In this paper, the dependence of adsorption, disjoining pressure isotherms and free energy of swelling on temperature and pressure is investigated by means of grand canonical Monte Carlo molecular simulations (GCMC).

2. Molecular simulation of crystalline calcium silicate hydrates

Classical Monte Carlo simulations in grand canonical ensemble are run as a function of the confinement (i.e. for different centre-to-centre or basal distance with respect to solid layers) and temperature. Interactions between the species are described by CSHFF force field [10] and SPC water model. The chemical potential of SPC water as a function of the temperature is obtained by means of thermodynamic integration of Gibbs-Duhem equation. Calcium counterions are added to the interlayer space in order to ensure the electroneutrality of the system. For each temperature and basal spacing, a simulation is run with Towhee [11] package using configuration bias methods. Each simulation is run during 30 million Monte Carlo steps (10 million steps for equilibration and 20 million for sampling). The convergence criterion adopted is a stable energy system (with the standard deviation of the total energy below 0.02 % of the mean value). The atomic structure of calcium silicate hydrate is derived

from Hamid's [12] structure of tobermorite 11 Å with molar Ca/Si ratio of 1: $Ca_6[Si_6O_{18}].2H_2O$. The cell parameters of the resulting monoclinic cell are a = 6.69 Å, b = 7.39 Å, c = 22.77 Å and γ = 123.49° [12]. Figure 1 shows snapshots of configurations at equilibrium associated to three basal spacings.

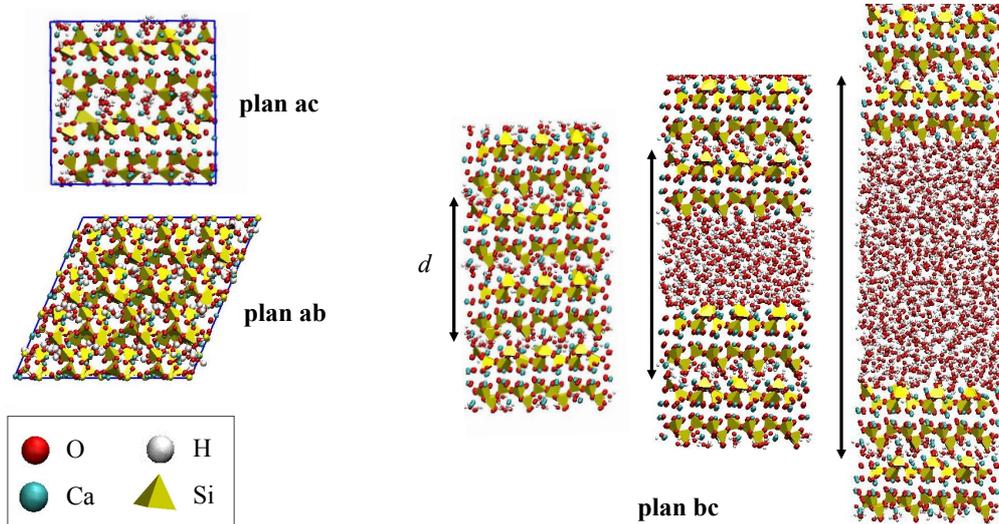
Figure 1: Snapshots of the (monoclinic) structure of Hamid's 11 Å tobermorite with Ca/Si = 1 and equilibrium configurations at three basal spacings d.
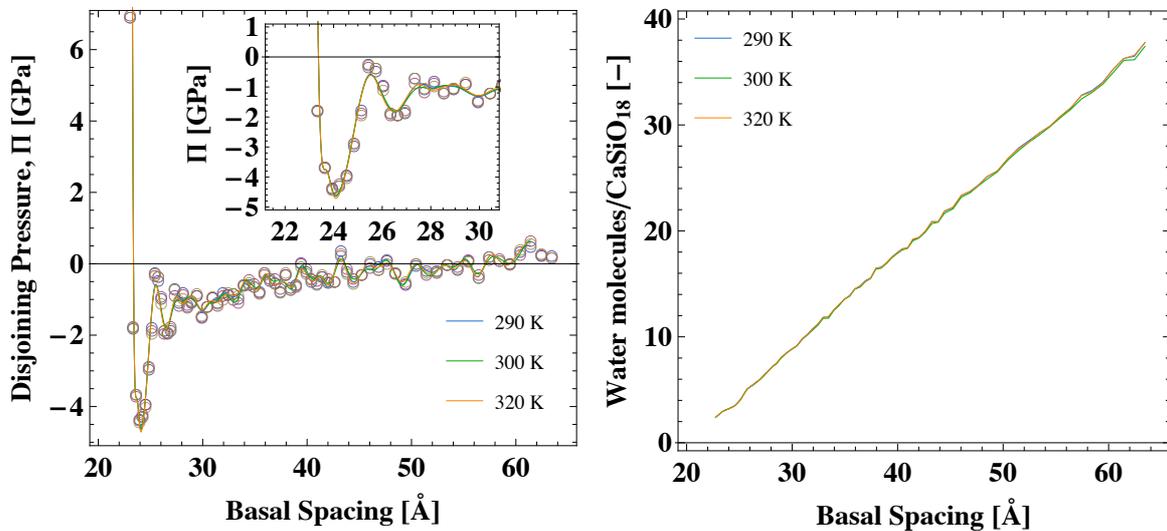

Figure 2: *At left*, disjoining pressure isotherms as a function of basal spacing for three temperatures. The inset shows the details of oscillation corresponding to the first hydration states. *At right*, adsorption isotherms as a function of basal spacing for the same temperatures.

4. Results and discussion

Figure 2 (left) shows the disjoining pressure isotherms according to the three temperatures. The disjoining pressure is the difference between the confining pressure and the fluid pressure $\Pi = P - P_w$. The effects of the temperature, in the temperature range considered, is not very pronounced. The confining pressure isotherms at 300 K are in agreement with other pressure isotherms reported in the literature [6, 7]. For small basal spacings, it is possible to identify the quasi-dehydrated (some water molecules remains trapped in the calcium silicate pores even for small basal spacings), in which the confining pressure strongly increases with the decrease in d as a result of the steric repulsion between the solid layers, counterions and the remaining water molecules. The oscillations corresponds to the various possible hydration states nW with water structuring in discrete n layers up to the state of pore water ∞W. The 1W hydration state can be clearly distinguished, as can be seen in the inset of Fig. 2. The distance between the oscillations (taking, for example, the minimum values in the inset of Fig. 2 as reference) is circa 3 Å, which roughly corresponds to the Lennard-Jones diameter of the oxygen in SPC water model. The portions of the curve in which the pressure increases with the basal spacing are instable. Therefore, the system is subjected to micro- or snap-through instabilities [13], which are reported to be at the heart of important phenomena in nanoporous materials such as shrinkage and creep. Figure 2 (right) reports the adsorption isotherms for the three temperatures. Again, the effect of the temperature in the range considered is not very pronounced.

Some key physical properties can be computed from the pressure isotherms. This information can be used to validate the output of the simulation [6]. Table 1 shows the out-of-plane elastic modulus $E_{zz} = -d_{eq} \frac{\partial \lambda}{\partial d}\Big|_{d_{eq}}$, surface energy $\gamma_s = -\frac{1}{2} \int_{d_{eq}}^{\infty} \lambda \, d(d)$ and cohesive pressure $P_{cohesive}$ (i.e. the pressure needed to disjoin two solid layers, which corresponds to the minimum in the pressure isotherms) computed at different temperatures. The estimates are compared against results from experiments and simulations reported in the literature and a fair agreement is observed.

Table 1: Physical properties computed from the confining pressure isotherms: validation against experimental and simulation results from the literature.

	Out-of Plane elastic modulus, E_{zz} (GPa)	Surface energy, γ_s (J/m^2)	Cohesive pressure, $P_{cohesive}$ (GPa)
This work:	79.7 (290 K)	1.07 (290 K)	4.18 (290 K)
	77.7 (300 K)	1.07 (300 K)	4.16 (300 K)
	79.9 (310 K)	1.05 (310 K)	4.22 (310 K)
Others	77.6 [6]; 61 [14]	0.67 [6]; 1.15 [19]	6.5 [6]
	89 [15]; 68.4 [16]	0.32-0.4 [17, 18]	5.0 [20]

Figure 3 shows the free energy of swelling as a function of the basal spacing: according to the temperature (left) and control pressure (right). The effect of temperature, in the range considered, is minor. The control pressure affects the depth of the potential well, or the total surface energy. The energy barriers associated with hydrate state transitions can be measured directly on these energy profiles. The energy profile concerning the system at 300 K was

fitted using the of generalized Lennard-Jones potential: $U_i(d) = 4\epsilon\left[\left(\frac{\sigma}{d}\right)^{2\alpha} - \left(\frac{\sigma}{d}\right)^{\alpha}\right]$, with $\sigma = 21.81$ Å, $\epsilon = 60.1 \times 10^3$ kJ/mol and $\alpha = 7.01$. This potential can be used to upscale calcium silicate hydrates behaviour at the mesoscale.
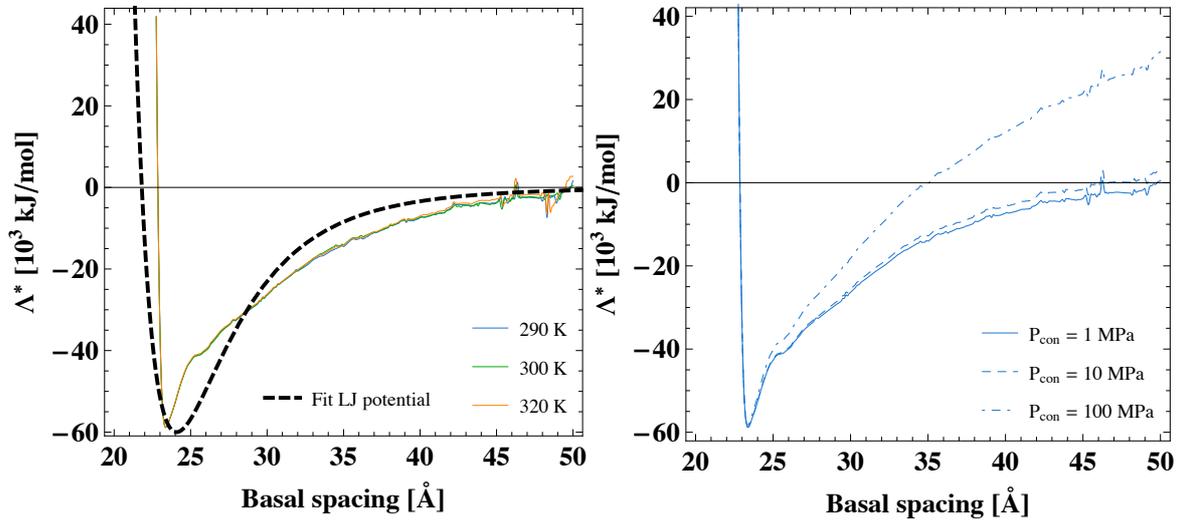

Figure 3: Free energy of swelling as a function of the basal spacing: according to the temperature (*left*) and control pressure (*right*). At left, the energy profile at 300K is fitted using the generalized Lennard-Jones potential.

4. Conclusion

In this article, the intermolecular interactions between crystalline calcium silicate hydrates were reported. These interactions result from the interplay between steric repulsion, attractive forces and depletion forces or entropic solvation, which lead to an oscillatory (non-convex) energy profile susceptible to manifest (snap-through) micro-instabilities. Here, these interactions were presented in terms of disjoining pressure isotherms and free energy of swelling. The convexification of the energy profile leads to the mesoscopic energy profile of a stack of solid layers in drained conditions. These results leave room to a better understating of the nature of water confined in calcium silicate hydrates nanopores (i.e. interlayer and gel pores). The derived energy profiles can be used to compute the interparticle interactions at a mesoscale (gel scale).

References

[1]   Pinson MB, Masoero E, Bonnaud PA, et al. Hysteresis from Multiscale Porosity: Modeling Water Sorption and Shrinkage in Cement Paste. Phys Rev Appl 3 (2015), 064

[2]   Acker P Swelling, shrinkage and creep: a mechanical approach to cement hydration. Mater Struct 37 (2004), 237–243

[3]   Sellevold EJ, Bjøntegaard Ø. Coefficient of thermal expansion of cement paste and

SynerCrete'18 International Conference on Interdisciplinary Approaches
for Cement-based Materials and Structural Concrete

24-26 October 2018, Funchal, Madeira Island, Portugal

concrete: Mechanisms of moisture interaction. Mater Struct 39 (2006), 809–815

[4]   Honorio T, Brochard L, Vandamme M. Effective stresses and estimations of the apparent Biot coefficient in stacked clay nanolayers. Géotechnique Lett (2018)

[5]   Honorio T, Brochard L, Vandamme M (2017) Hydration Phase Diagram of Clay Particles from Molecular Simulations. Langmuir 33 (2017), 12766–12776

[6]   Masoumi S, Valipour H, Abdolhosseini Qomi MJ. Intermolecular Forces between Nanolayers of Crystalline Calcium-Silicate-Hydrates in Aqueous Medium. J Phys Chem C 121 (2017), 5565–5572

[7]   Bonnaud PA, Labbez C, Miura R, et al. Interaction grand potential between calcium–silicate–hydrate nanoparticles at the molecular level. Nanoscale 8 (2016), 4160–4172

[8]   Wyrzykowski M, Mcdonald PJ, Scrivener K, Lura P. Water Redistribution within the Microstructure of Cementitious Materials Due to Temperature Changes Studied with 1H NMR. J Phys Chem C (2017)

[9]   Tambach TJ, Bolhuis PG, Hensen EJM, Smit B. Hysteresis in Clay Swelling Induced by Hydrogen Bonding: Accurate Prediction of Swelling States. Langmuir 22(2006), 1223–1234

[10] Shahsavari R, Pellenq RJ-M, Ulm F-J. Empirical force fields for complex hydrated calcio-silicate layered materials. Phys Chem Chem Phys 13 (2010), 1002–1011

[11] Martin MG. MCCCS Towhee: a tool for Monte Carlo molecular simulation. Mol Simul 39 (2013), 1212–1222

[12] Hamid SA. The crystal structure of the 11 Ä natural tobermorite Ca2.25[Si3O7.5(OH)1.5]·1H2O. Z Für Krist - Cryst Mater 154 (1981), 189–198

[13] Bazant ZP, Bazant MZ. Theory of sorption hysteresis in nanoporous solids: Part I. Snap-through instabilities. J Mech Phys Solids 60 (2012), 1644–1659

[14] Oh JE, Clark SM, Monteiro PJM. Does the Al substitution in C–S–H(I) change its mechanical property? Cem Concr Res 41 (2011), 102–106

[15] Oh JE, Clark SM, Wenk H-R, Monteiro PJM. Experimental determination of bulk modulus of 14 Å tobermorite using high pressure synchrotron X-ray diffraction. Cem Concr Res 42 (2012), 397–403

[16] Shahsavari R, Buehler MJ, Pellenq RJ-M, Ulm F-J. First-Principles Study of Elastic Constants and Interlayer Interactions of Complex Hydrated Oxides: Case Study of Tobermorite and Jennite. J Am Ceram Soc 92 (2009), 2323–2330

[17] Brunauer S. Surfaces of solids. Pure Appl Chem 10 (1965), 293–308

[18] Brunauer S, Kantro DL, Weise CH. The Surface Energy of Tobermorite. Can J Chem 37 (1959), 714–724

[19] Bauchy M, Laubie H, Qomi MJA, et al. Fracture toughness of calcium–silicate–hydrate from molecular dynamics simulations. J Non-Cryst Solids 419 (2015), 58–64

[20] Pellenq RJ-M, Lequeux N, van Damme H. Engineering the bonding scheme in C–S–H: The iono-covalent framework. Cem Concr Res 38 (2008), 159–174