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# **INFLUENCE OF THE FLEXIBILITY OF CALCIUM SILICATE HYDRATES LAYERS ON THE MESOTEXTURE: COARSE GRAINED SIMULATIONS ACCOUNTING FOR THREE-BODY INTERACTIONS**

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## **Abstract**

Calcium silicate hydrates exhibit various mesotextures, composed of fundamental pieces presenting with different morphologies. The structuration of nanolayer (2D) and nanofibrillar (1D) materials is a result of the interplay between intermolecular forces involving the fundamental pieces (layers or fibrils) and the pore fluid as well as the flexibility of each piece. In this paper, coarse-grained simulations are performed to simulate the differences in the mesotexture of crystalline calcium silicate hydrate with a fibril morphology taking into account the flexibility of these fibrils. The resulting pore size distributions of the gel are computed and exhibit a dependence on the size of the fibril. These results are a contribution to a better understating of C-S-H nanostructuration.

## **1. Introduction**

Calcium silicate hydrates exhibit a variety of morphologies, such as isotropic grains, 1D fibrils and 2D foils as well as in-plane dimensions, ranging from few tens of nanometers up to several micrometers [1]. For layers with large aspect ratio, the flexibility of the layers might play a role in the structuration of the material with important repercussion in the hygro-mechanical response of the material [2]. However, the effects of flexibility (or three body interactions) are not generally taken into account in simulations of the mesotexture of calcium silicate hydrates [3–5]. The structuration of nanolayered or nanofibrillar materials is a result of the interplay between intermolecular forces involving the fundamental “pieces” (layers of fibrils) and the pore fluid as well as the flexibility of piece. These intermolecular forces, or potential of mean force, can be computed by means of grand canonical simulations (c.f. the

paper “Interactions between crystalline calcium silicate hydrates: grand canonical simulation of pressure and temperature effects” presented by the author also in this conference). The flexibility of single layers of tobermorite (Hamid’s 11 Å tobermorite with Ca/Si=1 [6]) have been previously computed by the author [2]. The bending moduli in each orthogonal in-plane direction of the pseudo-orthorhombic cell are, respectively  $(4.68 \pm 1.74) \times 10^{-17}$  J and  $(1.42 \pm 0.91) \times 10^{-17}$  J [2]. These values are few orders of magnitude larger than (flexible) polymeric layers ( $\sim \times 10^{-20}$  J) and on the same order than other phyllosilicates such as clays [7]. With this bending modulus, tobermorite layers with more than few nanometers in one of the in-plane dimensions may potentially exhibit a bent configuration [2].

The flexibility of clays layers is recognized to play a major role on the structuration of the nanolayered materials. The reasoning can be, of course extended to nanofibrillar materials. Two limit cases can be compared [8]: (a) flexible or long layers or fibrils that are not prone to stack leads to entangled or spaghetti-like mesotextures, whilst (b) rigid or short layers or fibrils that are prone to stack leads to brick-like mesotextures. The resulting microstructure in (a) presents smaller pores (less permeable, therefore) and cohesion due to entanglement of a layer in different ordered domains, which may lead to a more ductile macroscopic behaviour. The resulting microstructure in (b) presents larger pores (more permeable) and granular behaviour, which may translate in a brittle macroscopic behaviour.

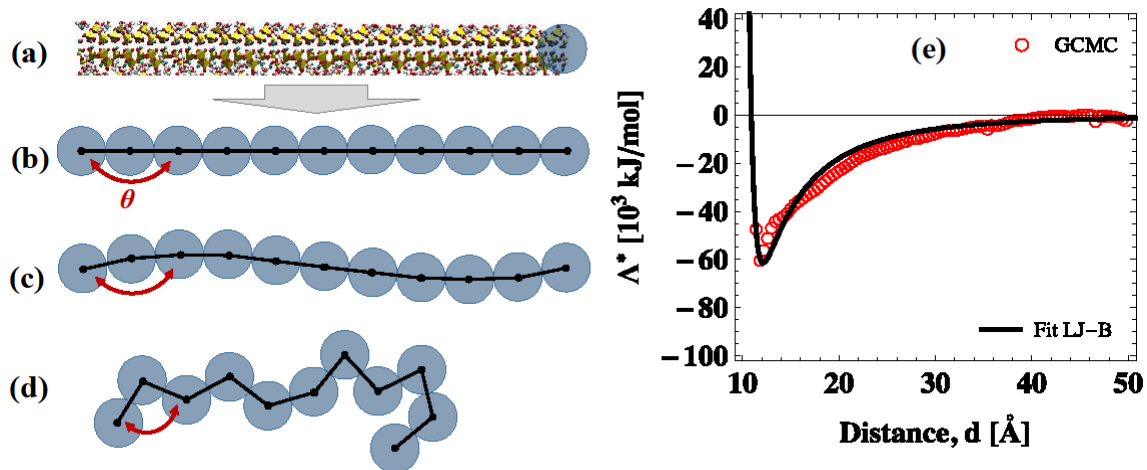


Figure 1. *At left*, Representation of a solid layer by a chain of spherical grains: (a) snapshot of the atomic structure of Hamid’s [6] 11 Å tobermorite with Ca/Si = 1; fibril representation with (b) large bending modulus (c) intermediary bending modulus (persistence length larger than the grain sizes) and (d) small bending modulus (the persistence length smaller than the grain size). *At right*, (e) potential of mean force obtained from grand canonical Monte Carlo simulation [9] and fitted LJ-B potential from a previous study.

In this paper, coarse-grained simulations are performed to simulate these differences in the mesotexture of calcium silicate hydrates. The potential of mean force and flexibility of a crystalline calcium silicate hydrate are considered. Three fibrils sizes and their propensity to stack are explicitly taken into account. The resulting pore size distributions for each scenario

are compared. These results are a contribution to a better understating of C-S-H nanostructuration.

## 2. Models and simulations

The atomic structure of Hamid's 11 Å tobermorite [6] with molar Ca/Si ratio of 1 is considered ( $\text{Ca}_6[\text{Si}_6\text{O}_{18}]\cdot 2\text{H}_2\text{O}$ ). This same structure was also studied by other authors interests in the meso-structuration of calcium silicates (e.g. [10, 11]). Figure 1 (a) shows the replicated monoclinic cell ( $a = 6.69 \text{ \AA}$ ,  $b = 7.39 \text{ \AA}$ ,  $c = 22.77 \text{ \AA}$  and  $\gamma = 123.49^\circ$ ) along a-axis, as proposed by Hamid [6]. The atoms in tobermorite are interacting via CSHFF [12], which is a force field based only in non-bonded Lennard-Jones interactions for metal and metalloids while harmonic bonds are only defined for water molecules and hydroxyls. This force field has been extensively used in the computation mechanical, thermal and interfacial properties of crystalline and disordered calcium silicates [13]. The surface charge density of the tobermorite layer is  $-0.55 \text{ C.m}^{-2}$ , which is close to the experimental value of  $-0.5 \text{ C.m}^{-2}$  [14].

### 2.2 Coarse-grained simulations accounting for two- and three-body interactions

The tobermorite solid layer is represented by a chain of spherical grain interacting *via* non-bonded forces (derived from the potential of mean force), two-body forces (derived from the in-plane elasticity of the solid layer) and three-body forces (derived from the bending modulus of the solid layer). The interaction between solid tobermorite layers and the fluid in drained conditions are detailed in another study [9]. These interactions are fitted by a generalized Lennard-Jones (LJ) potential combined with the Buckingham potential, as reported in Fig. 2, for all distances smaller than the cut-off distance  $d_c = 50 \text{ \AA}$ :

$$U_{LJ-B}(d) = 4\epsilon \left[ \left( \frac{\sigma}{d} \right)^{2\alpha} - \left( \frac{\sigma}{d} \right)^\alpha \right] + A \exp \left( -\frac{d}{\beta} \right) - \frac{C}{d^6} \quad \forall d < d_c \quad (1)$$

with  $\sigma = 5.907 \text{ \AA}$ ,  $\epsilon = 151.85 \times 10^3 \text{ kJ/mol}$  and  $\alpha = 2.85$ , for the LJ potential and  $A = 1.213 \times 10^{12} \text{ kJ/mol}$ ,  $\beta = 0.4670 \text{ \AA}$  and  $C = 0$ , for the Buckingham potential.

Bonds or two-body interaction are described by an harmonic bond:

$$U_{2-b}(d) = k_{2-b}(d - d_0)^2 \quad (2)$$

with force constant  $k_{2-b} = 939 \text{ kJ/(mol \AA}^2)$  computed from the elastic moduli according to the in-plane direction of the solid layer; and the equilibrium bond length distance  $d_0$ , corresponding to the effective thickness of the solid layer. In this study, the in-plane elastic moduli computed by first principles simulations [15], in Hamid 11 Å tobermorite with Ca/Si = 1, are used (i.e. 148.25 and 138.35 GPa). The equilibrium bond length adopted is  $d_0 = 11.81 \text{ \AA}$ .

Angles or three-body interaction described by a harmonic bond:

$$U_{3-b}(d) = k_{3-b}(\theta - \theta_0)^2 \quad (2)$$

where  $k_{3-b} = 11.44 \text{ kJ}/(\text{mol rad}^2)$ , is the bending modulus of the solid fibril and  $\theta_0$  is the equilibrium angle ( $180^\circ$  for a flat solid fibril). According to their flexibility and persistence length (parameter depending on the bending modulus), the fibril can assume different configurations (Fig. 1 right): from a flat surface (large bending modulus) to a crumpled configuration (small bending modulus).

The molecular dynamics simulations are performed with LAMMPS [16]. The fibrils are generated in a grid with a dilute concentration so that the distance between the fibrils is much larger than the cut-off of the non-bonded interactions. Circa 40000 grain are considered in each scenario. A velocity corresponding to 5000 K is randomly attributed to each individual grain. A 0.5 ns run in NVT ensemble is performed so that the fibril may assume random orientations. Then, the temperature is decreased to 300 K during 0.1 ns and equilibrated in this temperature during 0.2 ns. Next, the system is subjected to a pressure of 1 atm; an equilibration run of 0.5 ns is followed by the sampling of the configurations to be considered in pore size distribution analysis. The pore size distribution of the resulting mesotexture is assessed by means of the method developed by Bhattacharya et al. [17]. Three fibril size are considered  $N = 5, 10$ , and  $20$  grains, where  $N = L/d_0$  is the ratio between the largest dimension  $L$  of the fibril divided by the diameter of the grain  $d_g = d_0$ .

### 3. Results and discussion

Figure 2 displays the mesotextures obtained for the three fibril sizes considered. It is possible to identify only slightly bent configurations in all cases. In the cases treated here, the fibrils can be fairly approximated by rigid rods. This aspect highlights the importance of considering bending rigidity in modelling C-S-H.

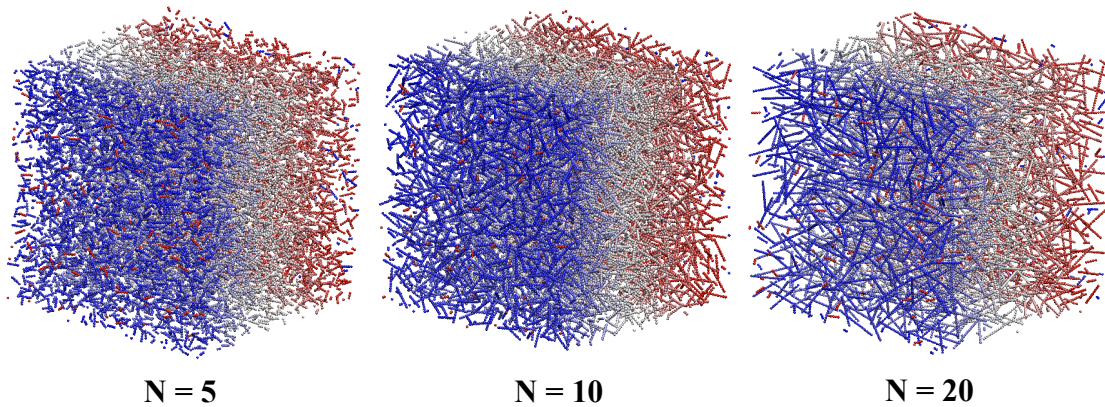


Figure 2. Mesotexture according to the size of the fibril: systems with 8000 ( $N = 5$ ), 4096 ( $N = 10$ ) and 1728 ( $N = 20$ ) fibrils, respectively (i.e. circa 40000 grains in each case).

The corresponding pore size distributions of the mesotextures are compared in Fig. 3. The range of pore sizes covered by the numerical samples corresponds to gel pores (0.5-10 nm)

and medium capillary pores (10-50 nm). The probability density function follows a normal distribution with average ( $\pm$  standard deviation) pore diameter of  $7.6 \pm 1.8$  nm ( $N = 5$ ),  $9.0 \pm 1.9$  nm ( $N = 10$ ) and  $9.1 \pm 2.2$  nm ( $N = 20$ ), respectively. For moderately flexible fibrils as tobermorite, increasing the fibril size leads to an increase in the average pore size and the standard deviation of the pore size distribution.

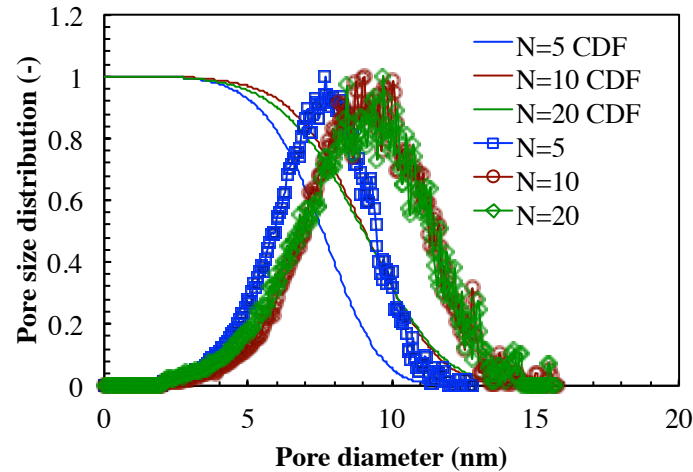


Figure 3 Differential and cumulative pore size distributions according to the size of the fibril (considering the bending modulus of tobermorite layer).

#### 4. Conclusion

In this paper, the effect of considering the flexibility (or three-body interaction) of solid fibrils on the mesotexture of calcium silicate hydrates is studied. Fibrils of tobermorite are moderately flexible in the sense that they can show some bent configurations for moderate loads on the order of the kPa up to the MPa [2], which can easily be found in cement-based materials [18]. The increase of fibril size translates in the increase of the probability of finding bent fibrils in the equilibrium configurations. In this study, only slightly bent configurations were observed even for the scenarios with the longest fibril ( $N = 20$ ). An increase in the fibril size, for a fixed bending modulus, leads to changes in the meso-structuration of calcium silicate hydrates: both the average pore size and the standard deviation of the pore size distribution increase with the size of the fibril. Future investigations will tackle with the structuration of 2D layers as well as combination of fibrils of different sizes.

#### References

- [1] Richardson IG. Tobermorite/jennite- and tobermorite/calcium hydroxide-based models for the structure of C-S-H: applicability to hardened pastes of tricalcium silicate,  $\beta$ -dicalcium silicate, Portland cement, and blends of Portland cement with blast-furnace slag, metakaolin, or silica fume. *Cem Concr Res* 34 (2004), 1733–1777
- [2] Honorio T, Brochard L. Flexibility of C-S-H sheets and stacks from molecular

- simulations. Second International RILEM/COST Conferene on Early Age Cracking and Serviceability in Cement-Based Materials and Structures, Belgium (2017)
- [3] Masoero E, Del Gado E, Pellenq RJ-M, et al. Nanostructure and Nanomechanics of Cement: Polydisperse Colloidal Packing. *Phys Rev Lett* 109 (2012), 155503
  - [4] Ioannidou K, Krakowiak KJ, Bauchy M, et al. Mesoscale texture of cement hydrates. *Proc Natl Acad Sci* (2016) 201520487
  - [5] Yu Z, Zhou A, Lau D Mesoscopic packing of disk-like building blocks in calcium silicate hydrate. *Sci Rep* 6 (2016)
  - [6] Hamid SA. The crystal structure of the 11 Å natural tobermorite  $\text{Ca}_{2.25}[\text{Si}_3\text{O}_{7.5}(\text{OH})_{1.5}] \cdot 1\text{H}_2\text{O}$ . *Z Für Krist - Cryst Mater* 154 (1981), 189–198
  - [7] Suter JL, Coveney PV, Greenwell HC, Thyveetil M-A. Large-Scale Molecular Dynamics Study of Montmorillonite Clay: Emergence of Undulatory Fluctuations and Determination of Material Properties. *J Phys Chem C* 111 (2007), 8248–8259
  - [8] Zabat M, Vayer-Besançon M, Harba R, et al. Surface topography and mechanical properties of smectite films. In: Rosenholm JB, Lindman B, Stenius P (eds) *Trends in Colloid and Interface Science XI*. Steinkopff, (1997) pp 96–102
  - [9] Honorio T. Interactions between crystalline calcium silicate hydrates: grand canonical simulation of pressure and temperature effects. Funchal, Madeira Island, Portugal (2018)
  - [10] 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
  - [11] Masoumi S, Valipour H, Abdolhosseini Qomi MJ. Interparticle Interactions in Colloidal Systems: Toward a Comprehensive Mesoscale Model. *ACS Appl Mater Interfaces* 9 (2017), 27338–27349
  - [12] 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
  - [13] Mishra R, Kunhi A, Geissbühler D, et al. cemff: A force field database for cementitious materials including validations, applications and opportunities. *Cem Concr Res.* (2017)
  - [14] Allen AJ, Thomas JJ, Jennings HM. Composition and density of nanoscale calcium–silicate–hydrate in cement. *Nat Mater* 6 (2007), 311–316
  - [15] 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
  - [16] Plimpton S. Fast Parallel Algorithms for Short-Range Molecular Dynamics. *J Comput Phys* 117 (1995), 1–19
  - [17] Bhattacharya S, Gubbins KE. Fast Method for Computing Pore Size Distributions of Model Materials. *Langmuir* 22 (2006) 7726–7731
  - [18] Honorio, T, Brochard, L, Bary, B. Statistical variability of mechanical fields in thermo-poro-elasticity: multiscale analytical estimations applied to cement-based materials at early-age. *Cem. Concr. Res* 110 (2018) 24–41