Multiscale Modelling of C-S-H from the force field to the Quantum Chemistry

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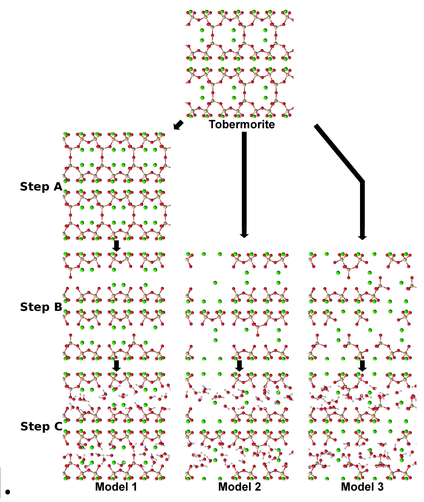
Structure of C-S-H (revised)

C-S-H (calcium silicate hydrate) is a nanocrystalline compound that is being created during the hardening of concrete. Understanding the atomic structure of C-S-H and its electronic properties is essential for improving macroscopic properties of concrete. During the last decade, several crystallographic models were proposed for C-S-H, but none of them can be verified by experiment. Recently [1,2] we constructed a set of periodic structures (containing more than thousand atoms) following the ideas form these crystallographic models. Due to the random character of creating defects in the structure and a freedom with positioning of water molecules, the total number of structures is astronomically large. Using subset of these crystal structures we performed MD simulations with ReaxFF [1] and semiempirical PM6 [2] calculations to confirm that the most stable structure corresponds to the model, suggested in [3]. The proposed structure (Model 1) is also better fit the experimental data (density, coordination numbers).



How crystals can grow? (and how to model it?)

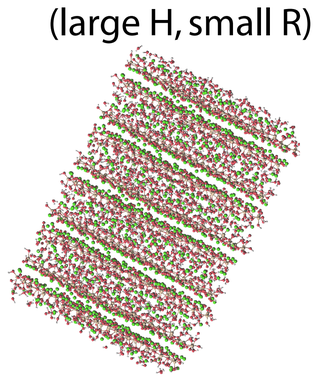
A distinctive property of C-S-H nano-crystals is a very anisotropic, pancake-like shape, where the size in Z-direction is much smaller than the size of the particle in XY direction. No explanation for anisotropy of C-S-H or limited size is given.

Crystal growth can be modelled by "adding a new block", but it is complicated:
- What is a next block?
- How to avoid unstable intermediates?
- How to include the surrounding (water)?

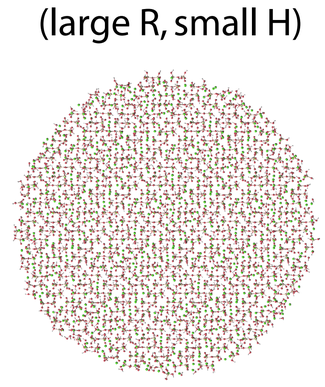
Shape and size of C-S-H nano particles

In order to explain this anisotropy we created a set of cylinder like particles of C-S-H and computed the total energy as a function of the dimension (Z and R) by using force field simulations (ReaxFF) and semiempirical methods (PM6). DFT is in a pipeline, but it is very time consuming.

Tower (large H, small R)

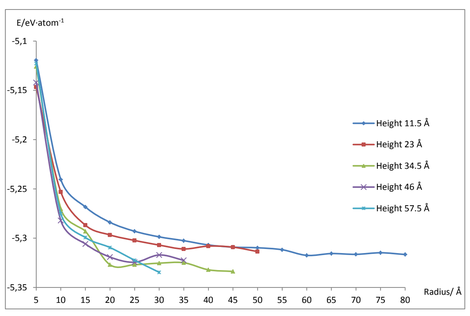


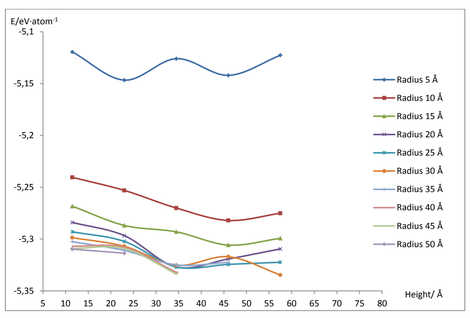
Pancake (large R, small H)



Timing for ReaxFF (LAMMPS) and PM6 (MOPAC) calculations for different sizes of C-S-H platelets.

SIZE		COMPOSITION				METHOD	
R	H	Si	Ca	O	H	ReaxFF	PM6
5	11.5	8	12	43	30	8″	7′
10	11.5	34	54	176	108	46″	4h15′
50	11.5	842	1377	4129	2136	28′	-
80	11.5	2072	3534	10503	5650	1h12′	-
5	23	17	28	90	56	18″	31′
50	23	1652	2769	8280	4414	1h01′	-
5	46	34	48	176	120	34″	5h
35	46	1640	2716	8198	4404	1h19′	-
5	57.5	40	63	220	154	55″	-
30	57.5	1482	2462	7451	4050	1h05′	-





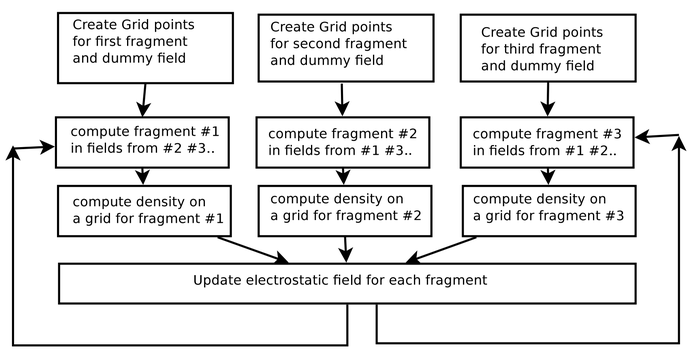
Energy change for the system with increase of radius (on the left) and height (on the right). Growth in Z direction is discrete due to the layered structure of C-S-H, and with no gain in energy. Growth in XY direction lower the energy (especially for small R).

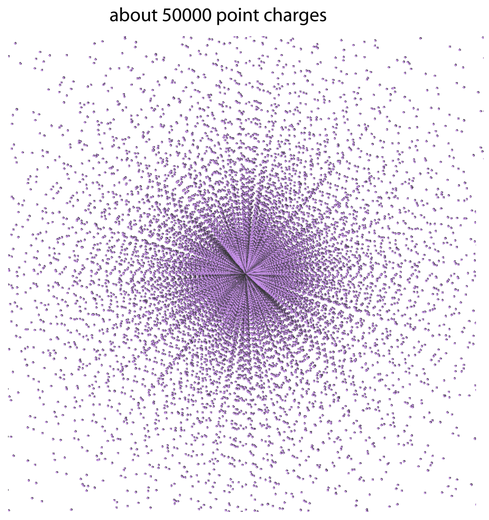
Final test is to compare Pancake and Tower for the same (almost) composition. The total energy for pancakes is always lower (both in vacuum and in water solution).

New embedding approach

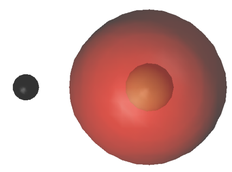
We developed a new fragment-based approach which can be used to model ionic crystals with any quality of the Hamiltonian. In this method, the true electronic density of the neighbouring fragments is obtained from ab initio calculation of a fragment. The procedure is automatic and it can be applied in a self-consistent way. The algorithm is implemented in Molcas [4], but can be easily extended . C-S-H is an ideal system for fragment approach: it contains isolated SiO tetrahedra (mostly dimers), water and CaO.

Self consistent procedure of fragment calculation

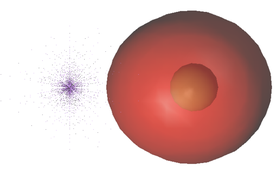




KF molecule
K is presented
by a point charge



a snapshot of
fragment calculation



References:

[1] G.Kovačević, B.Persson, L.Nicoleau, A.Nonat, V.Veryazov. Cement Concrete Res 67, 197 (2015)
[2] G.Kovačević, L.Nicoleau, A.Nonat, V.Veryazov. Z. Phys.Chem. (2016) (DOI: 10.1515/zpch-2015-0718)
[3] A.Nonat, Cement Concrete Res. 34, 1521 (2004)
[4] http://www.molcas.org