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Nano to Microlevel Modeling of Cement-Based Materials

by E.A.B. Koenders, J.S. Dolado, K. van Breugel, and A. Porro

Synopsis: Recent developments in nanotechnology paved the way for deepening the modeling level of science-based kernels and enabling new opportunities in terms of understanding the formation of hydration products and their contribution to the microstructure. Based on these developments next generation models are considered to have the potential to design new advanced materials that contribute to sustainable construction. One of the activities currently running in this field is the Codice (COmputationally Driven design of Innovative CEment-based materials) project which is a multi-scale modeling research project established within the European research arena FP7. The project has the ambition to bridge the nanoscale to the microscale by applying advanced computational simulation modeling techniques for cementitious materials. Nano-based models will be connected to the microscale level within the framework of the Hymostruc model. It is the objective of the CODICE project to provide more insight into the role of the fundamental building blocks of CSH gel (basically 5nm sized nanoparticles) and the mechanisms that govern their aggregation into high-density (HD) and low-density (LD) C-S-H varieties. Thus, the project aims to refine the microstructure of the Hymostruc model (Breugel 1991) so as to recognize the two types of C-S-H aggregates. The new computational scheme is expected to be a perfect tool to design new cementitious materials with improved mechanical properties.

Keywords: CSH gel; microstructure; modeling; nanotechnology.

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INTRODUCTION

Almost from the early start of the application concrete, the process of early hydration required the attention of many researchers. Already at the end of the eighteenth century, it was Tetmayer (1883) who was engaged with temperature measurements of early-age concrete. At the beginning of the nineteenth century, temperature effects in massive concrete structures were considered as a serious problem (Clover 1973). Onsite experimental programs were developed in order to control the concrete quality and to avoid unexpected harming of the concrete structure. Sometimes these experiments were supported by hand made temperature calculations and, based on this, early-age stresses and strength predictions were conducted. Substantial concessions had to be made regarding the interpretation of the mix design, properties, schematization and modeling approach. These concessions were related to the lack of knowledge about what was really going on inside the concrete and the fact that only very limited calculation tools and capacity were available that time. Those early days of modeling the hydrational behavior of cementitious materials are now definitely left behind. The pace of developments in the field of computational methods of hydration of cementitious materials has been tremendously. Nowadays, research results become available superfluously at a high rate and the availability of substantial computer power has become a common thing. Complex models used to analyze in-depth processes can be simulated at in an increasing level of detail. At this moment most computational models for cement hydration modeling have schematized the microstructure at he microlevel offering a clear picture of the processes that govern the hydration process of cementitious material. Albeit the final of modeling detail has not been reached yet, it still becomes clearer that the nano level is the level that has to be reached in order to be able to manipulate the original properties of a material. Many initiatives have been set in this field recently and others are already running to explore this particular field of science. A joined effort in this field is the EU CODICE project (CODICE 2008) titled “Computationally Driven design of Innovative Cement-based materials” and is developed within a consortium framework. The main objectives of the CODICE project are to develop serial parameter-passing multi-scale modeling schemes to monitor and predict:

- The (nano/micro)-structural formation and evolution of cementitious matrices as a function of macroscopic processing variables, such as the size of the cement grains, water/cement ratio, cement grain composition, etc.
- The degradation (aging) of cementitious structures subjected to osteoporosis-like chemical degradation processes, as a function of macroscopic processing variables.
- The mechanical performance of cementitious skeletons given their (nano/micro)-structure (accurate structure-performance linkage).

Without these joint efforts, it is considered to be impossible to make concrete a ‘predictable material’. The question arising from these numerical challenges will be discussed in this paper. First the basic concept of cement hydration is discussed followed by an historical overview addressing the developments of hydration models ending up with a list of the currently most used models in this field. Next the challenges in the field of nanotechnology will be discussed in view of the activities that run under the CODICE umbrella. Finally, the paper ends up with a retrospective view about computational modeling in view of the future ambitions and conclusions.

THE HARDENING PROCESS—THE BASIC CONCEPT

Cement can be considered as a granular material. The dimensions of the particles vary from 1 μm (0.000039 in.) up to about 100 μm (0.0029 in.). The particles are irregular shaped and exhibit a complex chemical composition. The most important phases identified within cement are the calcium silicates (C_3S and C_2S), calcium aluminate (C_3A) and calcium aluminate ferrite (C_4AF). When coming into contact with water, chemical reactions will commence while contributing to the formation of a solid microstructure. At first a short reaction will take place where a small percentage of the available C_3A will dissolve and reacts with the gypsum forming tricalcium sulfate. In addition, ettringite is being formed that possesses a needle shaped structure. These needles form a spatial framework in between the hydrating cement particles (Fig. 1, stage a and b). With ongoing hydration, the spatial framework will be occupied gradually by means of the development of calcium silicates hydrates (C-S-H gel). These silicate hydrates are formed close to the surface of cement particles. At the same time, crystal shaped calcium hydroxides are formed that likely precipitate in water rich spaces. During the process of hydration, reaction products are being formed with the property that the volume of the reaction products is smaller than the volume of the original reactants. This volume reduction is generally known as chemical shrinkage and is contributing to densify the reaction products. As the thickness of the shell of hydration products surrounding a hydrating cement particle is increasing, it is becoming more and more difficult for ions to diffuse through this shell and to pass the distance towards the anhydrous cement grain, or the other way around. The cement reaction becomes diffusion controlled and is retarding the overall rate of reaction of the hydration process (Fig. 1, stage c and d).

TOWARDS HYDRATION MODELS

Over the years, researchers have proposed models that were able to simulate the progress of the hydration process and could be used as a basis to estimate the associated properties. In this respect, the single particle model of Pommersheim (1980) can be considered as one of the most advanced approaches for simulating the hydration of tricalcium silicate hydrate. In these days, Pommersheim distinguished different kinds of hydration products viz. the 'inner product', the 'middle layer' and the 'outer product' (see Fig. 2). The middle layer is considered to be a layer which goes into solution and which is hard to penetrate. The inner and outer products are considered to have different densities with a different diffusivity resistance. With the use of basic numerical techniques, the rate of degeneration of the middle layer and the diffusion coefficients of the inner and outer products could be tuned in such a way that an accurate 'fit' for the experimentally determined hydration curves could be reached. However, this model didn't address the effect of the particle size distribution.

With the simulation model HYMOSTRUC (Breugel 1991), Van Breugel developed a full particle-based microstructural simulation model that accounts explicitly for the particle size distribution, the chemical composition, the water-cement ratio and the hydration temperature. The model follows a statistical basis for the inter-particle distances and calculates the formation of microstructure according to a so-called particle embedding mechanism. The model can be used to calculate a virtual microstructure and enables the possibility to calculate the associating material properties. Figure 3 shows an example of a simulated virtual microstructure (water/cement = 0.3) at three different stages of the degree of hydration, i.e. α_h = 0%, 20%, and 50%. In the simulations are carried out for cement, particles are 'stacked in space' at random locations. The cubic sample includes particles with diameters ranging between 1 and 37 μm (0.000039 and 0.00145 in.).

Still the most advanced operational hydration model is the model developed by Bentz and Garboczi (1991) at NIST. In the beginning of the nineties they introduced the pixel-based model called CEMHYD3D. A cementitious microstructure is considered to be built up from elements, called pixels, representing a volume of 1 μm^3 (1.31×10^{-12} yd^3). Initially, cement grains are stacked at random in a 3-D space or a digitized scan of a microstructure is used as the simulations' initial state. At the boarders of the cement grains, pixels go into solution and optionally react with other pixels under the formation reaction products. CEMHYD3D is a fundamental model and suitable to examine the hydration process at the microlevel. At this moment, new initiatives are being exploited at NIST and focus on the hydration model that has its roots at the nano scale level, called HydratiCA (Bullard 2009). This model incorporates schemes for the basic chemical and physical processes for simulating the hydration process (Fig. 4).

NANOSCALE SIMULATION

With the European CODICE project it is the ambition to introduce nanotechnology in simulation models for cement hydration and to make these advanced technologies applicable for the construction sector. Within the framework of a model, nanotechnology-based models for C-S-H gel formation will be implemented and connected

to the microlevel model Hymostruc by using a multiscale modeling approach. Research activities take place at the nano-, sub-nano, and the microlevel. Emphasis is on modeling C-S-H gel formation and the (re)use of this information at the microlevel to increase the modeling accuracy and to be able to predict more advanced materials properties as well. The basic structure of the CODICE project is provided in Fig. 5. The tasks of CODICE exhibit a clear interconnectivity, showing clear feedback at a threefold level:

- Firstly at the level of the formation, hydration and evolution of cementitious skeletons, in which there is a clear feedback between the multi-scale modeling of the formation and evolution of cementitious skeletons and the experimental validation of the formation of cementitious skeletons.
- Secondly at the mechanical performance of the cementitious skeletons, in which there is an analogous feedback between multi-scale modeling of the "bearing capacity" of the cementitious structures and its experimental validation of the performance of the computationally-driven designs.
- Finally, the project has a third loop connecting formation, hydration and evolution and mechanical performance, accounting for the fact that wise designs must be guided by structure-performance linkages.

With regard to the CODICE project it is stressed that different iterations are planned to feedback the microstructures' mechanical performance. The starting criterion that links the microstructure to its performance will be the most appealing designs that correspond to those with lower (micro)-porosities and higher volume fractions of the C-S-H gel.

DOWNSCALING MICROSTRUCTURE

When considering the geometrical gap between the micro and the nano level it has to be noticed that 3 orders of magnitude have to be downscaled. The microstructural-based models like those being implemented in Hymostruc or the NIST model CEMHYD3D have common working dimensions of 100 x 100 x 100 μm^3 (0.0039 x 0.0039 x 0.0039 in.) (see Fig. 5) representing a microstructure built up from anhydrous cement particles, hydration product (inner and outer) and a capillary pore structure. By bridging the gab with the nanolevel the microlevel sample has to be downsized and the interface with the nano level has to address the physical and chemical processes that are active on the much smaller scale level (see Fig. 6). In this respect, nano-based numerical models simulate the formation of C-S-H gel and the formation of hydration products at the atomistic level. When upscaling this information and considering the microlevel models as the level to connect to, it can be observed that the formation of hydration products at the microlevel model becomes visible in terms of the inner and outer hydration products. With the simulation of the formation of hydration products at the nanolevel and upscaling this information towards the microlevel, a much more detailed view on the morphological formation of chemical bindings can be taken into account. In Fig. 6 this are the shells that surround the anhydrous grains and mimics the formation of hydration products. The products that grow in outward direction account for the formation of structure, i.e. represented by the relative amount of chemical bindings. Besides, the formation of hydration products at the nanolevel, it also provides the opportunity to pave the way for the development of cementitious materials possessing new or improved properties and complying with the requirements of the client to a larger extent. It is a way toward the development of a multi-scale computational model for the design of tailor made cementitious materials.

NANOLEVEL CHALLENGES

Albeit the C-S-H gel constitutes the main ingredient of cementitious skeletons and their life-service depends crucially on it, the possibility of tuning the intrinsic nature and properties of the C-S-H gel has been simply out of reach. Fortunately this long-standing impossibility can be currently overcome by the complementary action of new experimental capacities and stronger simulations schemes which explicitly pay attention to the nanoscale. Recent nanoindentation experiments (Acker 2001; Constantinidis 2004) have revealed that the C-S-H gel can present itself either in a low stiffness and low density variety (called LD C-S-H gel) or in a variety with a high stiffness and high density (called HD C-S-H gel). This dissimilar bearing capacity is indeed much more pronounced in their resistance to osteoporosis-like degradation processes. The question that arises is straightforward: Could the formation of the stronger and more durable HD C-S-H varieties be promoted over the LD- ones?

It must be admitted that at present, our knowledge on C-S-H gel is too vague so as to realistically face such a challenge. Our incomplete picture of C-S-H gel basically relies on two complementary visions, each one oriented to explain different sizes and phenomena (see Fig. 7). One the one hand, several works have centered their analysis on the recognition of the structural features of C-S-H gel at the molecular level. It is well recognized that C-S-H gel exhibits a short-ordering alike to that of distorted tobermorite and jennite crystals (Taylor 1984; Richardson

1992; Cong 1998) (Fig. 7(a)). On the other hand, other strain of research has paid attention to the recognition of the colloidal properties of C-S-H gel (Powers 1960; Sereda 1970; Wittmann 1979). Current model is the Jenning's model (Jennings 2000). This model basically considers that the C-S-H gel is composed of approximately 5 nm (0.0000002 in.) sized rounded particles, which, in turn, aggregate to form high-density (HD) C-S-H or low-density (LD) C-S-H depending on a packing factor (Fig. 7(b)).

Unfortunately it is still unclear nowadays how to link the short-ranged structures with the colloidal particles. It is clear, therefore, that an ineludible prerequisite prior to any realistic technological possibility is to obtain further knowledge on the short-range ordering of C-S-H particles the colloidal models start from; namely we need to change our current picture of these basic C-S-H bricks (based on ~5 nm [0.0000002 in.] sized particles) by an improved version which accurately accounts for their real morphology and chemistry.

In this scenario, any hint on the structure of C-S-H gels that can be given by modeling and numerical simulations would be tremendously beneficial. Although atomistic simulations have been barely applied to deal with C-S-H gel, there is lately a great agreement that they represent an unmatched opportunity to unravel the smallest features of C-S-H gel. Some progress has been made so far. For instance, it is worth noting that recent Molecular Dynamic (MD) simulations have reproduced many important features of the cementitious C-S-H gels (the mean chain length, number of Ca-OH and Si-OH bonds, etc.) that, up to now, were only inferred from experiments (Dolado 2007). These calculations must be taken as an appropriate starting point for more accurate descriptions which could predict the sizes and shapes of the smallest C-S-H features as a function of the composition. Lets note that though Small Angle Neutron Scattering (SANS) experiments (Allen 2007) seem to be consistent with the 5 nm (0.0000002 in.) sized particles Jenning's model refers to, other techniques support other sizes and morphologies. From Atomic Force Microscope (AFM) measurements Nonat (2004) and Plassard (2004) suggest that the basic C-S-H bricks are 60 x 30 x 5 nm (0.0000024 x 0.0000012 x 0.0000002 in.) particles, whereas based on Transmission Electron Microscopy (TEM), Richardson (2004) recognizes 3 to 8 nm (0.00000012 to 0.00000032 in.) globular particles within the so-called Inner product (Ip) and thin particles of and variable length and about 3 nm (0.00000012 in.) in their smallest dimension within the Outer product (Op). Our feeling is that MD simulations are on the verge of identifying the basic C-S-H bricks and bridging the existing gap between the structural and colloidal visions of C-S-H gel.

Once the basic building blocks (BBB) of C-S-H gel are identified through MD simulations, the link with the aforementioned hydration models could be feasible by invoking the granular nature of C-S-H gel (Constantinidis 2007). After defining a "resolution" length L (~ 500 nm [0.00002 in.]), which is accessible to the microscale models, a sub-microscale piece of C-S-H gel (of generic $C_{na}S_{nb}H_C$ stoichiometry) can be refined by taking advantage that it basically consists of aggregations or repetitions of n BBBs (of generic $C_aS_bH_\Omega$ stoichiometry and size a_{BBB}), as schematically depicted in Fig. 8. Hence, different computational techniques can be (a priori) easily implemented so as to refine the structures derived from the hydration models. Differently to above mentioned MD simulations, which explicitly accounts for the atomic composition of the basic building bricks, the foreseen computational schemes might directly work with the basic particles. The simplest approach might be the use of Packing Algorithms (PA), which are very efficient computationally speaking but neglect the physical and chemical aspects of packing. Alternatively one might resort to Monte Carlo simulations where chemical reactions could intervene by defining appropriate inter-particle potentials. One possibility is to this end is the employment of the insights gained from MD simulations to define C-S-H particles decorated on their surfaces by appropriate Si-OH and Ca-OH bonds. The main drawback of both the PA and the MC simulations is that they provide useful information about the equilibrium configuration but say nothing about the kinetical and dynamical aspects of the aggregation process. Much more physical but much less computationally efficient methods like Distinct Element Methods (DEM) or Brownian Cluster Dynamics (BCD) could be used whenever the dynamical aspects are required.

Finally, it should be remarked that the above described nano-refinement of the microstructure can also be employed to determine the elastic properties of the cementitious skeletons. One possibility rests on solving the continuum linear elastic equations over Representative Elementary Volumes (REV) by means of standard Finite Element Model (FEM) or Finite Volume Model (FVE) simulations, in which the elasticity matrix $\{D_{el}\}$ at the nodes are provided by sub-micro and nano-scale simulations (see Fig. 9). After dividing a REV of side L_{REV} into voxels, the hydration models can be employed to say the actual chemical (or crystalline) composition of the voxel (C_3S, C_2S, Aft, C-S-H, etc.). With this knowledge, the elastic matrix at a point X ($\{D_{el}\}_X$) can be calculated through nano-simulations which give the intrinsic Young modulus E and Poisson ratio ν of the voxel. Lets note that recent atomistic simulations have been already able to predict both the intrinsic elastic properties of the most important

crystalline phases present in cement paste and even the experimental range observed for the stiffness of C-S-H gel once the intrinsic nanoporosity and the finite chain length of the silicate chains are properly accounted for (Manzano 2009).

CONCLUSIONS

With the CODICE project, it is the ambition to answer computational challenges that are required when bridging the gab between nano- and micro-scale modeling of cementitious materials by means of advanced computational simulations. In fact CODICE project aims to develop a serial parameter-passing multi-scale modeling scheme to predict the structural evolution and the mechanical performance of non-degraded and degraded cementitious matrices as a function of macroscopic processing variables to guide the design of cementitious materials in which the HD-C-S-H forms are promoted over the LD- C-S-H ones.

CODICE's computational toolkits expected to boost the competitiveness of the European Construction sector, since it will provide valuable and affordable tools to:

- Optimize the processes of cement production and to minimize its environmental impact.
- Decrease significantly the time and the costs of the quality control assessments.
- Enable the possibility to design new advanced sustainable materials.
- Provide flexibility in the use of performance design mixtures for the construction sector.
- Optimize the design of cementitious materials (either in terms of their mechanical performance or their life-cycle analysis).

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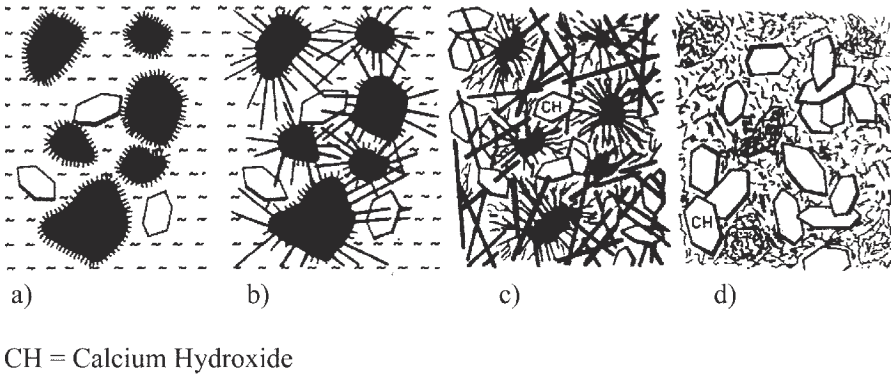

Fig. 1—Development of structure in cement-based materials (schematic, after Locher 1976): (a) plastic phase; (b) "setting" phase; (c) basis skeleton; and (d) stable skeleton.

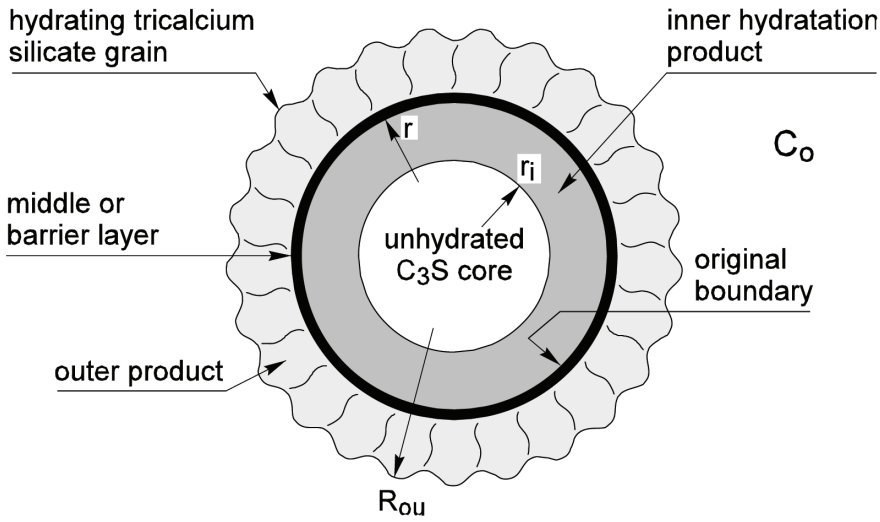

Fig. 2—Single particle model for hydration of tri-silicate according to Pommersheim (1980).

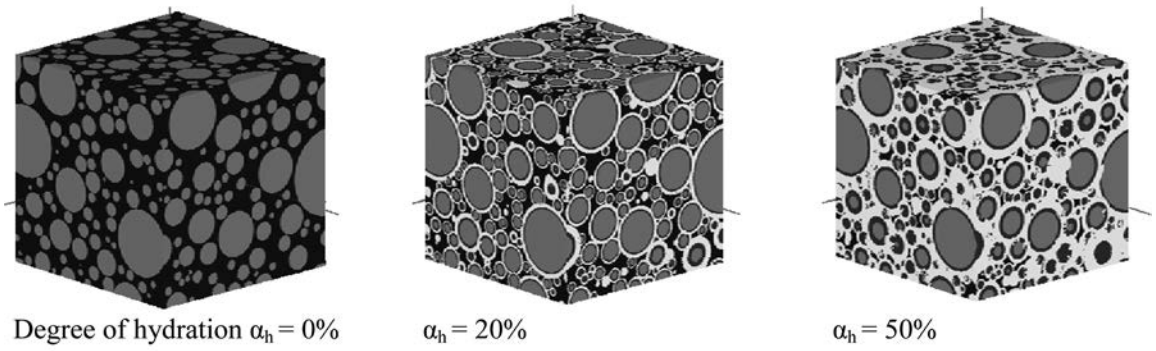

Fig. 3—Virtual microstructures of cement paste for three different stages of the hydration process, that is, $\alpha_h = 0$, 20, and 50%, simulated with Hymostruc (Breugel 1991). Water-cement ratio = 0.3.

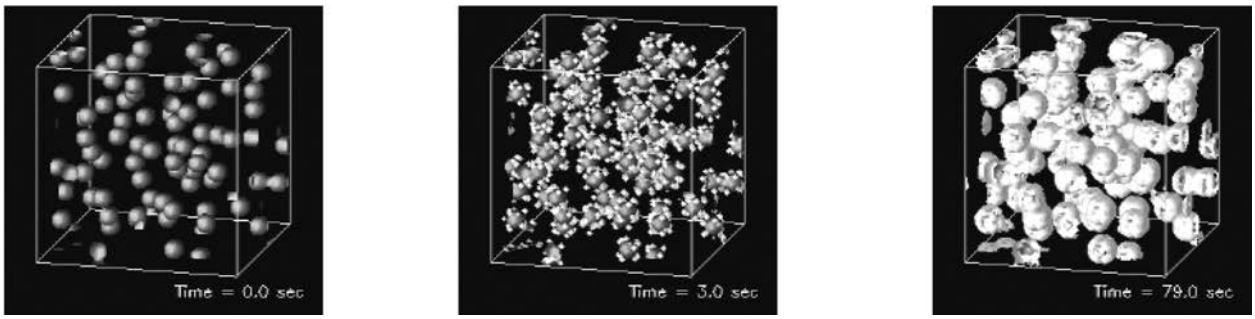

Fig. 4—Impression of a simulation conducted with the HydratiCA model (Bullard 2009).

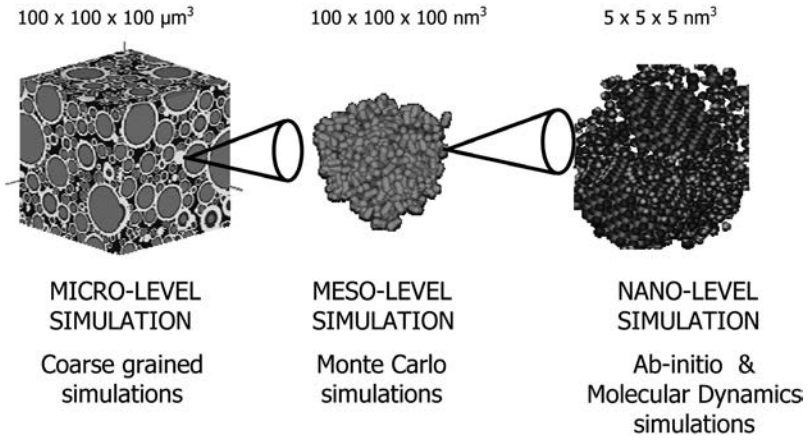

Fig. 5—Schematic impression of the multi-scale modeling approach conducted within the CODICE project.

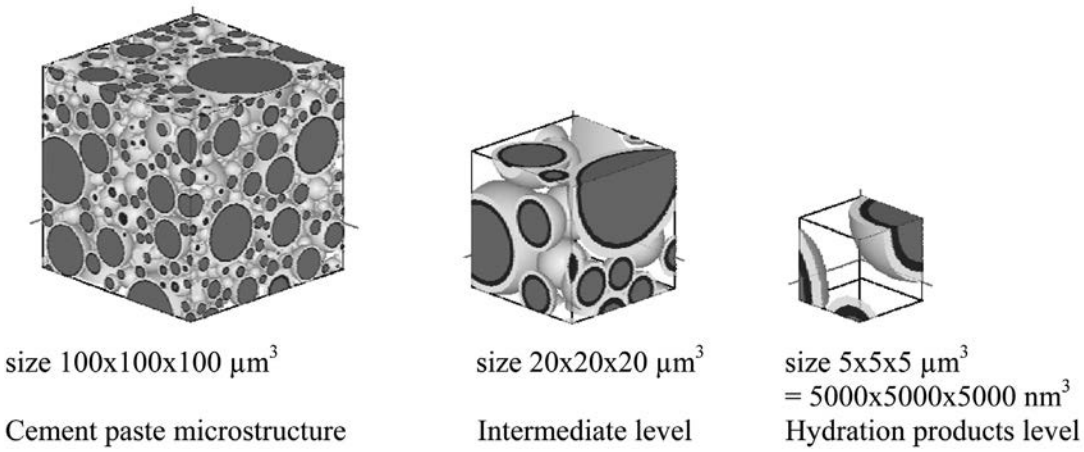

Fig. 6—Downscaling the virtual microstructure from the microlevel toward the nanolevel.

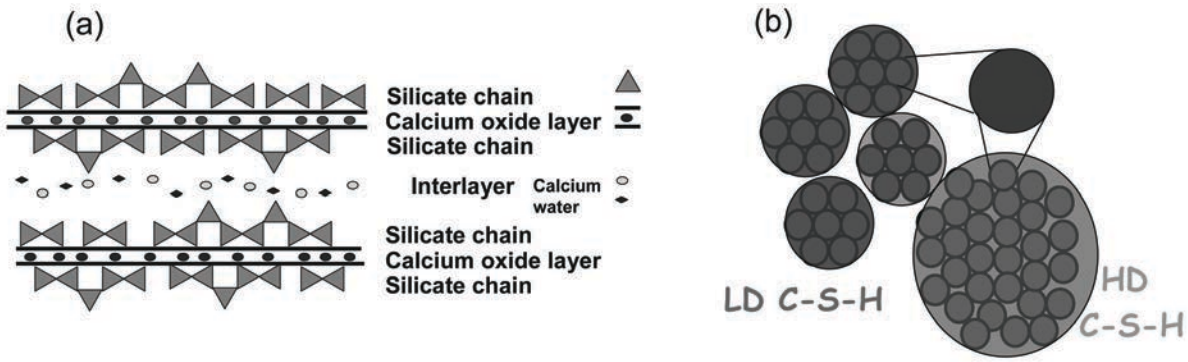

Fig. 7—Schematic representation of the two main visions for C-S-H gel: (a) structural model that describes the atomic scale of the C-S-H gel as an imperfect and disordered crystalline calcium silicate; and (b) colloidal model for the arrangement at the nanoscale of C-S-H gel nanoparticles.

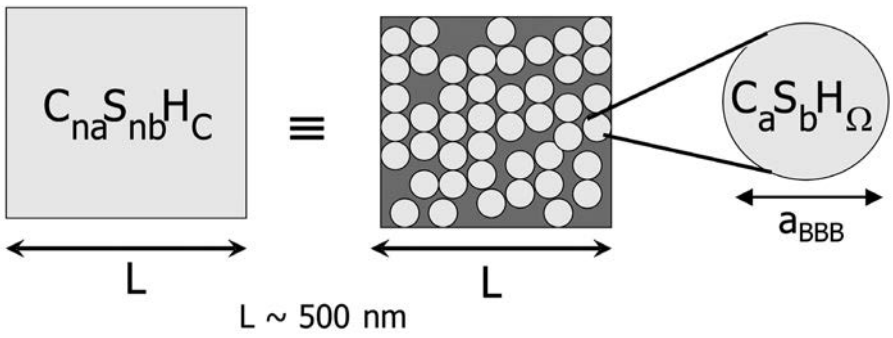

Fig. 8—Bridge from the microstructure and nanostructure. Note that as an appealing first approach, the Ca/Si of the BBBs can be taken as the same that the one appearing at the micro-level.

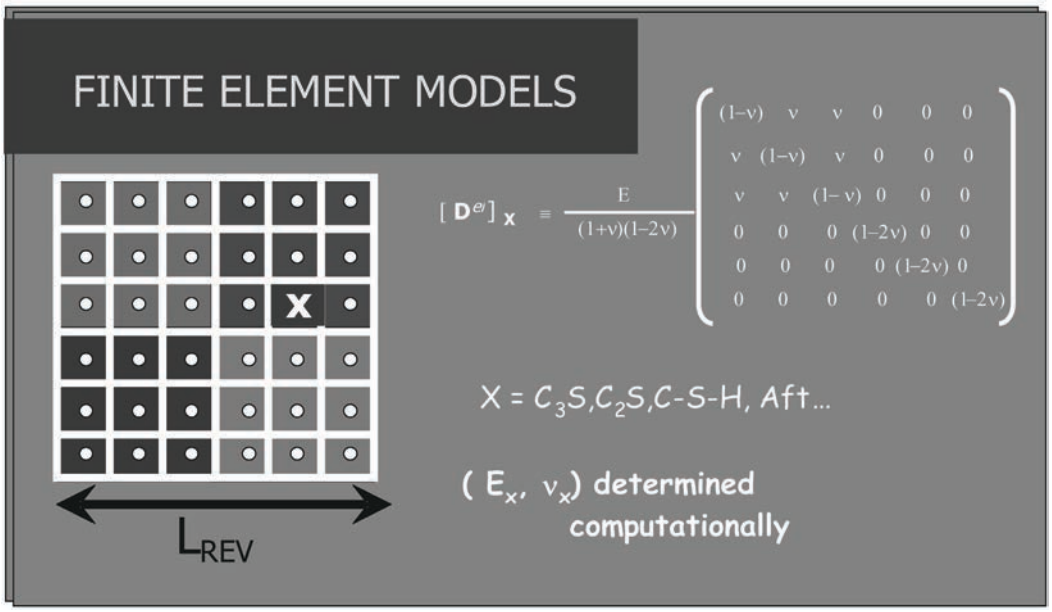

Fig. 9—One possibility to calculate the elastic properties of cementitious skeletons is based on finite element models, where the inputs at the nodes account for the nanostructure.