Non Equilibrium Molecular Dynamics simulation of the Hydrodynamics in Crystalline Calcium Silicate Hydrates Nanopores

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NON EQUILIBRIUM MOLECULAR DYNAMICS SIMULATION OF THE HYDRODYNAMICS IN CRYSTALLINE CALCIUM SILICATE HYDRATES NANOPORES

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Abstract

The processes associated with the hydrodynamics in calcium silicate hydrates nanopores are crucial to durability and confinement performance of concrete. We report Non Equilibrium Molecular Dynamics (NEMD) simulations of forced flows in crystalline calcium silicate hydrates nanopores. For slit pores larger than 4 nm, Poiseuille flow is observed for an imposed force parallel to both orthogonal directions of the basal plane. This result shows that Navier-Stokes, which is *a priori* restricted to the realm of continuum mechanics, can provide, even for nanopores, a reasonable description of the flow provided the adequate boundary conditions are employed. This observation go towards a better comprehension of water and aqueous solution transport phenomena in cement-based materials.

Keywords: Non Equilibrium Molecular Dynamics; Viscosity; Slip Boundary Conditions; Poiseuille flow.

1.   INTRODUCTION

The understanding of the physical phenomena governing the dynamics of water at the nanometric scale is crucial to predict the behaviour of micro- and meso-porous materials such as calcium silicate hydrates. Regarding cement-based materials, water transport phenomenon is critical to performance specifications related to the durability and the confinement capacity of the material.

Nanopores are one of the main pore size classes in cement-based materials. Water confined in nanometric pores is recognized to exhibit a different behaviour from bulk water due to adsorption and depletion forces resulting from the interaction with the solid surfaces. alters the structure and dynamics of confined.

Molecular simulations have been extensively used to assess the particularities of confined water within various nanoporous materials [1–3], including calcium silicate hydrates [4–6].

Water ordering adjacent to solid surfaces that is pore-size dependent is observed in crystalline calcium silicate hydrates [7]. Also, as for other nanoporous materials [2,8], confinement is recognized to deaccelerate water dynamics leading to a sub-diffusion behaviour and heterogenous diffusion [9].

On the other hand, hydrodynamics under forced flow at the nanoscale may exhibit the characteristics of ("macroscopic") Poiseuille flow, i.e. parabolic velocity profiles, in some nanoporous materials such as clays [10].

In this work, the hydrodynamics in calcium silicate hydrates under forced flow is studied using Non Equilibrium Molecular Dynamics (NEMD). To the best of the author's knowledge, this is the first time NEMD is used to assess forced flow in calcium silicate hydrates nanoporous. Velocity and density profiles are computed for 4 pore sizes. The viscosity of the fluid is computed using two approaches. The results are validated against experimental and simulation data concerning the viscosity of water. These results contributes to a better understanding of water transport in calcium silicate hydrates.

2.   MOLECULAR MODELS AND METHODS

We consider the atomic structure of Hamid 11 Å Tobermorite with a Ca/Si ratio of 1, which corresponds to the structural formula $[CaO][SiO_2][H_2O]_{0,5}$. The species in the system interact via CSHFF empirical force field [11]. Slit pores are constructed as detailed by Honorio [7] and filled with water via Grand Canonical Monte Carlo (GCMC) simulations for a system in equilibrium with an external water reservoir at 300 K and under 1 atm for pore sizes up to 4.2 nm. Figure 1(a) shows the snapshot of an equilibrium configuration obtained by GCMC simulations of tobermorite with a pore size of H = 0.8 nm .For pores sizes exceeding 1 nm, the number of water molecules scales linearly with the pore size (Fig. 1(c)), which allows extrapolating the water content of pores larger than nm. Figure 1(b) shows the equilibrium configuration of the H = 8 nm pore.

To simulate forced flow in tobermorite nanopores, NEMD simulations are performed. These simulation consist in applying a constant force $F = 0.75 \times 10^{-3}$ (kcal/mol)/Å = 5.21×10^{-5} nN to each fluid atom in the direction of the flow. We test both orthogonal direction of the basal plane (named here x and y). Similar simulation protocol and simulation parameters have been employed to study clays [10]. The temperature of 300 K was ensured via the rescaling of velocities and the thermostating was performed taking only the in-plane direction orthogonal to the forced flow into account. SHAKE algorithm was used to rigidify SPC water molecules. Periodic boundary conditions are applied. Ewald summation with a precision of 10^{-5} in forces was used to account for long-range electrostatic interactions.

We performed the simulations with LAMMPS code [12] using a 1 fs time step. Velocity and density profiles were computed per chunks defined by binning along the thickness of the slit pore and averaged during 0.1 ns blocks. A simulation not exceeding 2 ns was enough to reach steady state flows for the pore sizes considered here. Then, the system was sampled during at least 5 ns in order to get the velocity and density profiles.
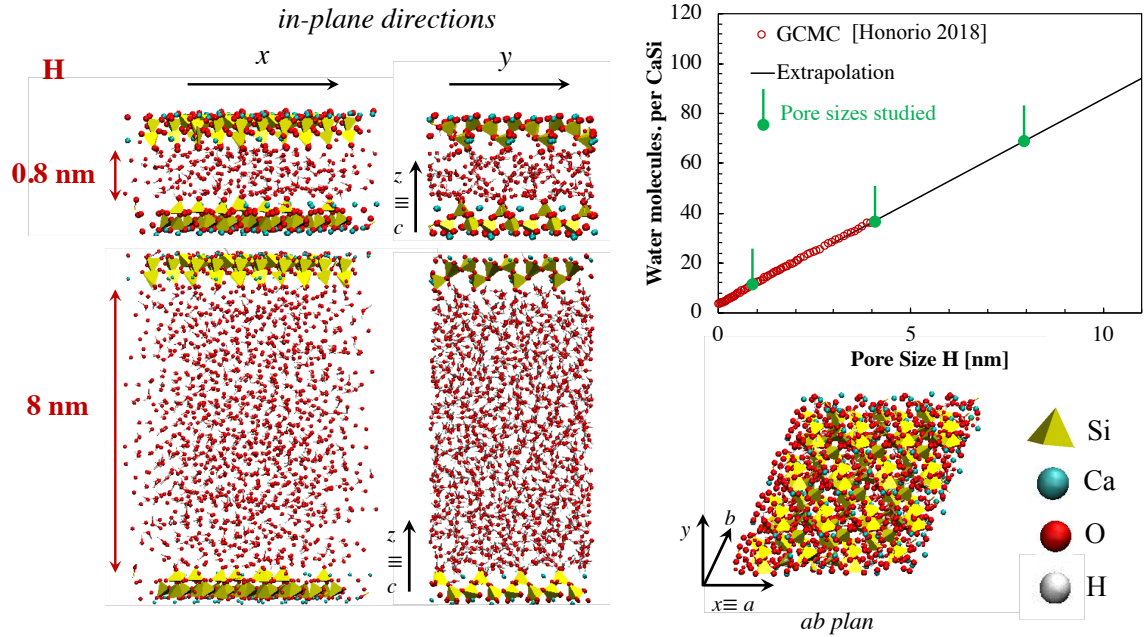
Figure 1: At the left, snapshots of equilibrium configurations of nanoporous tobermorite-water system with pore sizes H = 0.8 nm and H = 8 nm. At the top right, water isotherm at 300 K and under 1 atm of nanoporous tobermorite as a function of the pore size: GCMC simulations and extrapolation.

3.   RESULTS AND DISCUSSION

Figure 2 shows the velocity and density profiles for both orthogonal direction of the basal plan according to the four pore sizes studied. The velocities profiles obtained for both in-plane orthogonal directions are equivalent for all pore sizes. This result shows that the anisotropic surface roughness of tobermorite does not affect water dynamics, even for pores as small as 0.8 nm, which roughly corresponds to a three water layer according to the definitions of interfaces in [7].

Poiseuille flows (i.e. parabolic velocity profiles) are observed for the pores sizes of 4.2 and 8 nm. NEMD simulations on clays show that Poiseuille flows can be identified from pores larger than 3 nm [10]. Confinement effects significantly affects the hydrodynamics in 0.8 nm nanopores so that no parabolic velocity profiles are observed for this pore size. Density profiles of 0.8 nm nanopores shows denser packing of water molecules when compared to larger pore sizes.

The density profiles exhibit a marked oscillatory feature in the vicinity of the solid surfaces. These oscillations are due to water ordering adjacent to these surfaces as discussed in Honorio [7]. At distances z exceeding 1 nm from the solid surface, these effects are not significant and the water reach a density closer to the density of bulk water at 300 K and under 1 atm (approximately 1000 kg/m^3). In the portions of the pore the pores that are distances larger that 1 nm form the solid surface, velocity profiles are parabolic.
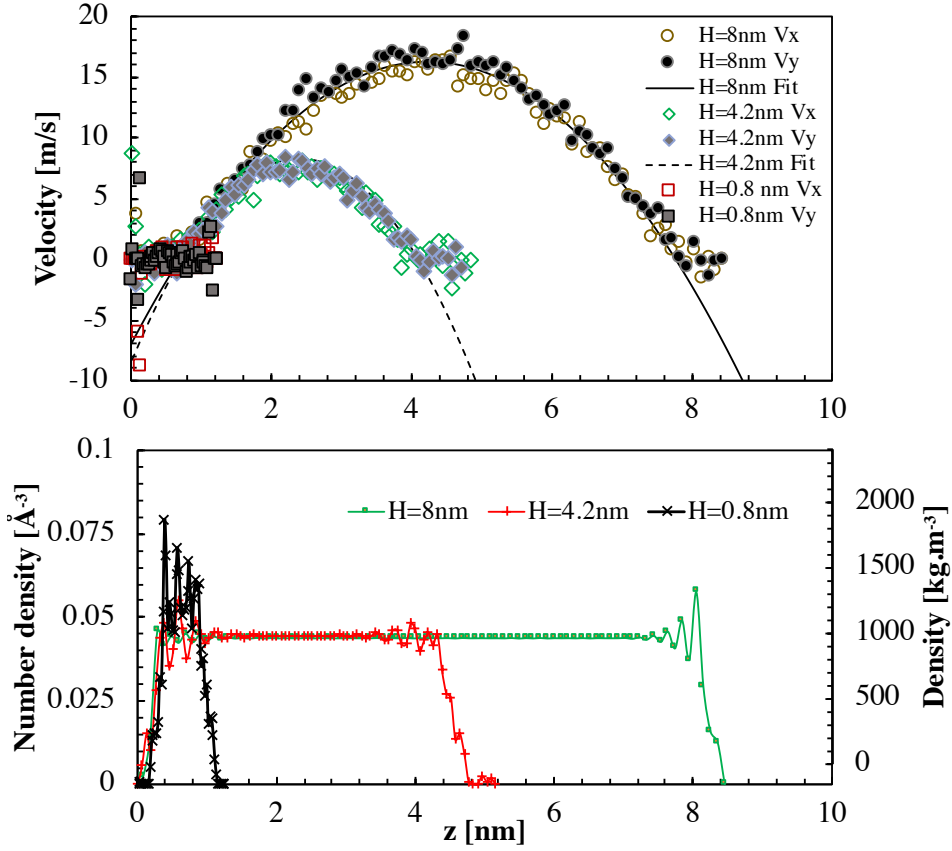
Figure 2: Velocity and density profiles for tobermorite-water system with pore sizes H = 0.8, 4.2 and 8 nm.

An estimation of the water viscosity η can be obtained from these velocity and density profiles using the expression [10]:

$$\eta = -F\rho_V \left(\frac{d^2v}{dz^2}\right)^{-1} \tag{1}$$

where ρ_V is the number density. The estimations of water using this expression are compared with the viscosity of SPC water and experimental viscosity of water at 300 K and 1 atm in Table 1. Our results are consistent with the values reported in the literature, which corroborates the validity of the results in Fig. 2.

The usual *stick* boundary conditions, which corresponds to a zero velocity at the interface fluid-solid, does not apply to the studied system, as can be readily seen from Fig. 2. In this context, a slip boundary condition can be defined based on the specific position z_I of the fluid-solid interface and a slip length b :

$$b = \pm V(z_I) \left(\frac{dV}{dz}\right)_{z_I}^{-1} \tag{2}$$

Different theoretical approaches can be employed to determine z_I [10]. The simplest one is to set z_I as the distance from the fluid-solid interface in which the fluid can be considered as behaving like a bulk fluid, that is the distance of approximately 1 nm as discussed above. Using

z_I = 1 nm, the slip length b = 2.8 Å (H = 4.2 nm) and 2.5 Å (H = 8.0 nm). These values are larger than the slip length of 2.1 Å computed to clays using different theoretical approaches to determine z_I [10]. Since the roughness of tobermorite solid surface is larger than the roughness of swelling clays (montmorillonite), the slip length of tobermorite it is expected to be larger than the slip length of clays.

Table 1: Viscosity of water: comparison against data from the literature

	Viscosity η [cP]	Reference
This work (Eq. 1)	0.79 (H = 4.2 nm) 1.1 (H = 8nm)	-
SPC water SPC/E water	0.58 0.67	[13] [10]
Experimental	0.85	[13]
SPC/E water in clay nanopores	0.70 (H = 4.5nm) 0.68 (H = 6nm) 0.709 (H = 8 nm) 0.685 (H = 10 nm)	[10]

11. CONCLUSIONS

Non Equilibrium Molecular Dynamics simulations were performed to study the hydrodynamics in crystalline calcium silicate hydrates nanopores. We conclude:

– Poiseuille flow is observed in slit pores larger than 4 nm for an imposed force parallel to the basal plane. In smaller pores, due to interface effects and water ordering, density and viscosity are not constant. This is also true to the first nm from the fluid-solid interfaces for all pore studies here.

– Regarding the pore allowing Poiseuille flows, the velocity profiles in both in-plane orthogonal direction are equivalent. Therefore, the anisotropic roughness of tobermorite surface does not affect significantly the flow within slit pores larger than 4 nm.

– Stick boundary conditions are not adapted to describe the Poiseuille flow observed in larger tobermorite nanopores. Slip boundary conditions with a slip length of approximately 2.65 Å can be used to correctly describe this Poiseuille flow.

– These results show that the simplest form of Navier-Stokes equation (i.e. with a homogeneous fluid fully characterized by its bulk viscosity and density) can provide a reasonable description of the flow provided the adequate boundary conditions are employed. This observation is particularly interesting because it points out the transferability of continuum fluid mechanics results to the nanoscale.

The perspectives of this work includes developing homogenization strategies that allows upscaling the hydrodynamics information from the nanoscale up to the scale of industrial applications of concrete.

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