

Toward a unified fluid/solid DFT-based formulation to describe multiphysics couplings appearing in nanoporous materials (confinement effects, adsorption-induced swelling and water phase changes)

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Abstract

In recent years, a major attention has been paid on nanoporous materials – characterized by the presence of some pores of nanometric size (below 100nm) – due to their importance in many applications such as gas storage and separation, catalysis, drug delivery, etc. Among them, one can find synthetic or natural materials such as zeolites, MOFs, activated or natural carbons, clays, tight rocks, cementitious or biomaterials, etc. These materials can trap an important quantity of molecules due to the high fluid-solid and fluid-fluid interactions occurring in these confined spaces. This results in an important modification of the properties of these fluids which can no longer be described by the classical tools used in bulk phases. Thus, a thermodynamic theory adapted to these inhomogeneous fluids must be used to describe the changes in density, pressure, phase equilibrium shifts, etc.

Among the existing theoretical developments, the molecular density functional theory (DFT) has emerged as one of the most powerful and convenient molecular approach for the description of the thermodynamic properties of inhomogeneous fluids. The development of DFT for classical fluids originates in the late 70's and its use is nowadays widespread for the description of fluid interfaces or fluids confined in nanopores, the characterization of porous materials, the analysis of freezing/melting transitions in simple fluids as well as in colloidal dispersions, etc. The success of DFT approaches is explained by the fact that they preserve detailed information on the microstructure of inhomogeneous fluids but with a much lower computational expense than molecular simulations.

In addition, the high molecular packing of the fluid at pore scale may induce significant consequences at the macroscale, such as instantaneous swelling which may be critical in different context, and which cannot be described by standard poromechanics introduced by Biot 75 years ago. Generally, natural and synthesized porous media are composed of two kinds of porosities: a microporosity (pore sizes below 2 nm) where the fluid is trapped as an adsorbed phase and a meso or a macro porosity required to ensure the transport of fluids to and from the smaller pores. If adsorption in nanopores induces instantaneous deformations at a higher scale, the matrix swelling may close the transport porosity, reducing the global permeability of the porous system or annihilating the functionality of these materials.

First, we will briefly recall the basic concepts of adsorption in nanoporous materials from both the modeling and experimental point of view. Particularly, we will illustrate the capabilities of a DFT formulation for the modelling of adsorption of different gases (CH_4 , CO_2 , water) and we will highlight specific features appearing in nanoporous materials (fluid confinement, pore pressure, phase changes).

Then, an extended poromechanical framework is presented allowing the prediction of adsorption-induced swelling deformation. Coupled with DFT, the model allows to consider the full pore size distribution of a porous media to predict adsorption-induced swelling and porosity changes. The model is validated by experimental comparisons on an activated carbon and on a natural coal extracted from a mine with enhanced coal bed methane recovery potentialities.

Finally, current studies and perspectives are presented for both the modeling of water crystallization effect and the estimation of elastic properties of solids solely based on DFT modeling leading the path toward an upscaling-based poromechanical framework that integrates DFT descriptions of both fluids and solids.

Vitae



David Grégoire (Full Professor in Mechanics), specialised in failure, transport properties and multiphysics couplings in porous media, has been graduated from ENS Cachan (France) in 2004. He obtained his PhD degree in Mechanics from INSA-Lyon (France) in 2008 and then joined Northwestern University (USA) as a research associate. After one year, he came back in France for a second postdoctoral position at UPPA where he was finally hired in 2010 at the ISA BTP civil engineering school. He defended his French habilitation thesis in Mechanics in 2014 and is heading since 2015 the Mechanics and Physics in Porous Media (MPPM) research group at LFCR (UMR5150). From 2010 to 2015, he was recipient of a CNRS Higher Education Chair and he is an honorary member of the Institut Universitaire de France (junior chair 2017-2022). From 2019, David Grégoire is co-heading the International hub Newpores dedicated to the mechanics and physics of porous materials, which intends to answer to new Energy and Environment challenges. This is a joint effort of the MPPM research group at UPPA (France), the Centre for Sustainable Engineering of Geological and Infrastructure Materials (SEGIM) at Northwestern University (USA), the University of Vigo (Spain), the Technical University of Madrid (Spain) and the University of Liège (Belgium).