Estimation of adsorption-induced pore pressure and confinement in a nanoscopic slit pore by a density functional theory

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Abstract This study aims at characterising the adsorption-induced pore pressure and confinement in nanoscopic pores by molecular non-local density functional theory (DFT). Considering its important potential industrial applications, the adsorption of methane in graphitic slit pores has been selected as the test case. While retaining the accuracy of molecular simulations at pore scale, DFT has a very low computational cost that allows obtaining highly resolved pore pressure maps as a function of both pore width and thermodynamic conditions. The dependency of pore pressure on these parameters (pore width, pressure and temperature) is carefully analysed in order to highlight the effect of each parameter on the confined fluid properties that impact the solid matrix.

Keywords Pore pressure · Adsorption · Microporous · Density functional theory · Methane · Carbon

1 Introduction

Following the IUPAC recommendation [1,2], the pore space in porous materials is divided into three groups according to the pore size diameters: macropores of widths greater than 50 nm, mesopores of widths between 2 and 50 nm and micropores of widths less than 2 nm. Zeolites, activated carbons, tight rocks, coal rocks, source rocks, cement paste or construction materials are among microporous materials. In recent years, a major attention has been paid on these microporous materials because the surface-to-volume ratio (i.e., the specific pore surface) increases with decreasing characteristic pore size. Consequently, these materials can trap an

1 The term nanopores is sometimes preferred in the Mechanics community to label pores of width less than 2 nm. However, the 2015 IUPAC report [2] recommends that this term embraces the three categories of pores, but with an upper limit $\approx$ 100 nm.

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important quantity of fluid molecules as an adsorbed phase. This is important for applications in petroleum and oil recovery, gas storage, separation, catalysis or drug delivery.

In very small pores, the molecules of fluid are confined (molecular packing). This effect induces that fluid–fluid and fluid–solid interactions sum at the pore scale and have significant consequences at the macroscale, such as instantaneous swelling or shrinkage deformation. In different contexts, these deformations may be critical. A lot of natural and synthesised porous media are composed of a double porosity: the microporosity 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 synthesised materials. Particularly, in situ adsorption-induced coal swelling has been identified [3,4] as the principal factor leading to a rapid decrease in CO₂ injectivity during coal bed methane production enhanced by CO₂ injection. Conversely, gas desorption can lead to matrix shrinkage and microcracking, which may help oil and gas recovery in the context of unconventional petroleum engineering [5]. The effects of adsorbent deformation on physical adsorption have also been identified [6] as the major challenge concerning gas porosimetry in nano-porous non-rigid materials (e.g. metal organic frameworks). In conclusion, there is now a consensus in the community that major attention has to be focused on the coupled effects appearing at the nanoscale within microporous media because they may have significant consequences at the macroscale [7].

Experimentally, different authors tried to combine gas adsorption results and volumetric swelling data (see e.g. [7] for a review). Pioneer works of Meehan [8] showed the effect of carbon dioxide sorption on the expansion of charcoal but only mechanical deformations were reported and no adsorption quantities were measured. Later on, different authors [5,9–14] highlighted the phenomenon on bituminous coals, because it is of utmost importance in the context of CO₂ geological sequestration and coal bed reservoirs exploitation. Recently, Perrier et al. [15,16] performed simultaneous measurements of adsorbed quantities and induced strain on an activated carbon and showed that the volumetric swelling is directly linked to the excess adsorbed quantity.

As far as modelling is concerned, standard poromechanics [17,18] links the macroscopic strain to the total stress and the pore fluid pressure (i.e. the bulk pressure in that case) and has led to relevant descriptions of various multiphysics phenomena in macroporous materials. However, this classical approach fails in describing adsorption-induced strain and predicts volumetric shrinkage instead of volumetric swelling for these microporous materials [19]. Such classical framework needs to be extended to take into account the fluid confinement effects present within the nanopores. In particular, molecular packing induces a deviation of the pore fluid pressure from its bulk value, the difference being most often denoted as solvation force or pressure [20]. The effect of this modified pore fluid pressure on the pore walls has to be characterised at the pore scale and up-scaled to represent macroscopic swelling strain. Molecular simulations are the classical tools to represent the distribution of molecules due to fluid–fluid and fluid–solid interactions at the nanoscale. Different authors used Monte Carlo simulation tools to study the pore fluid pressure profiles within nanopores. Do and co-workers performed Grand Canonical Monte Carlo simulations for argon [21,22], methane and methanol [23] in slit-shaped micropores with movable solid layers to compute the pore pressures and corresponding deformations. Kowalczky and co-workers studied adsorption-induced deformation of microporous carbons filled with carbon dioxide [24,25] and near-critical argon [26]. These investigations showed that pressures applied on the pore surfaces may be very high (few hundred of MPa), depending on the thermodynamic conditions and on the pore sizes. However, even if macroscopic adsorption isotherms may be reconstructed in a consistent way from molecular simulations through the material pore size distribution [27], molecular simulations are not a tractable nor an efficient tool to predict resulting deformations at a macroscale in a complex material. Hence, enhanced poromechanics framework have been developed [16,19,28,29] to obtain semi-analytical efficient and tractable tools capable of predicting macroscopic strain induced by adsorption in homogeneous microporous materials. In these formulations, the fluid confinement is macroscopically deduced from experimental measurements of adsorbed quantities and not from the thermodynamic state of the fluid at the nanoscale. For micro-to-macro heterogeneous porous media, the fluid confinement cannot be deduced from experimental measurement and new strategies have to be proposed.

If molecular simulations are too time consuming to be coupled with poromechanical models or macroscopic numerical simulations, an elegant and relevant alternative approach consists in estimating the fluid confinement with a molecular density functional theory (DFT).² It has been already shown [32,33] that non-local DFT is as accurate as molecular simulations to estimate density profiles of real fluids in nanopores but with a very lower

² A comprehensive description of DFT and its applications can be found in the review of Evans [30] or the monograph of Davis [31].