Estimation of the confinement state of methane and water 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). 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 here for methane in order to highlight the effect of each parameter on the confined fluid properties that impact the solid matrix. Additional results for water will be presented at the conference.

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 [1] of widths less than 2 nm.

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 has significant consequences at the macroscale, such as instantaneous swelling or shrinkage deformation. The effects of adsorbent deformation on physical adsorption has also been identified [3] 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 [4].

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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 ≈ 100 nm.

As far as modeling is concerned, standard poromechanics [5, 6] 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 [7]. Such classical framework needs to be extended to take into account the fluid confinement effects present within the nanopores. Especially, 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* [8]. The effect of this modified pore fluid pressure on the pore walls has to be characterized at the pore scale and upscaled 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. However, even if macroscopic adsorption isotherms may be reconstructed in a consistent way from molecular simulations through the material pore size distribution [9], 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 [7, 10, 11, 12] to obtain semi-analytical efficient and tractable tools capable to predict 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 [15, 16] that non-local DFT is as accurate as molecular simulations to estimate density profiles of real fluids in nanopores but with a very lower computational cost. Another key feature is that DFT is written in a continuum framework and then may be coupled more easily with continuum poromechanics theory than discrete simulations results. Balbuena *et al.* [17] proposed a theoretical study based on DFT to estimate the solvation pressure of Lennard-Jones fluids in slit micropores. At low pressure and low temperature conditions, Neimark and co-workers [18, 19, 20] or Ustinov and Do [21] used different DFT variations to estimate the solvation pressure (*e.g.* for porous media characterisation purposes). To our knowledge, only one article in the literature proposes to apply this strategy on a large range of temperature and pressure [22] by studying the adsorption of methane on natural coals at geological conditions.

This paper aims at using a non-local density functional theory combined with a powerful equation-of-state in order to obtain highly-resolved pore pressure maps as a function of bulk pressure and pore width at different temperatures. The proposed method allows to better characterise the complex pore pressure behaviour for large thermodynamic conditions on the whole range of micropore widths even for complex fluids. This is the first step to provide a unified theory from nano to macro scales that links adsorption of the fluid in the nanopores to the macroscopic deformation of the material.

Only the global strategy is presented in this paper. For further details, the reader may refer to reference [23].

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2. A comprehensive description of DFT and its applications can be found in the review of Evans [13] or the monograph of Davis [14].
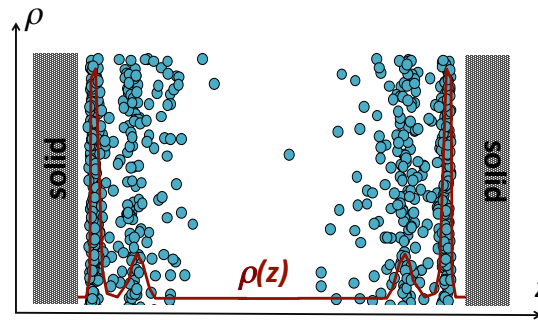
FIGURE 1 – Schematic view of a slit pore filled with methane. Reproduced from [23].

2 Theory

The version of the Non-Local Density Functional Theory (NLDFT) used in this work has been fully described in Malheiro *et al.* [15]. Therefore, the discussion on this theory will be limited to its most significant features here.

Let us consider a fluid of chemical potential μ at temperature T in a volume V. In the density functional theory (DFT) framework [13], the grand thermodynamic potential Ω of an inhomogeneous fluid in an external field in the grand canonical ensemble (μ, V, T) is given by :

$$\Omega[\underline{\rho}] = A[\underline{\rho}] - \sum_{i=1}^{N} \int_V \rho_i(\underline{x})[\mu_{bi} - V_i^{ext}(\underline{x})]dx \ . \tag{1}$$

In Eq. (1), Ω is the grand thermodynamic potential, A is the Helmholtz free energy, $\underline{\rho} = (\rho_1, ..., \rho_N)$ is the vector of the different molecular densities of the N species of the inhomogeneous fluid, which depend on the position vector $\underline{x}$, V_i^{ext} is an external field (e.g. a fluid/solid interaction potential), μ_{bi} is the bulk chemical potential of the specie i.

The minimization of this grand potential leads to the Euler-Lagrange equations that allow computing the density distributions of the fluid at equilibrium :

$$\frac{\delta\overline{\Omega}[\rho]}{\delta\rho_i} = \frac{\delta\overline{A}[\rho]}{\delta\rho_i} - \mu_{bi} + V_i^{ext} = 0 \qquad \forall i \in [1, N] \ . \tag{2}$$

In Eq. (2), $(\overline{\Omega}, \overline{A}$ are the volumetric grand thermodynamic potential and the volumetric Helmholtz free energy respectively.

In this work, the SAFT-VR equation of state [24] has been used as the thermodynamic model to compute both the properties of the bulk fluid phase and the chemical potential at equilibrium and as the bulk limit to build the inhomogeneous Helmholtz free energy. In this paper, we deal with methane, a fluid of non-associating spherical monomers of diameter σ, with a mean-field (MF) approximation, *i.e.* the correlations due to the long-range attractive interactions are neglected (see [23] for details).

In the following, we are considering a slit pore of width L made of two solid parallel graphitic surfaces and filled with methane (see Fig. 1). The external potential V^{ext} applied on the fluid is the sum of the Steele's interaction potentials [25].

As shown in Malheiro *et al.* [15], molecular simulations have been used to validate the methane's density profiles obtained with the NLDFT framework presented above in the full micropores range.
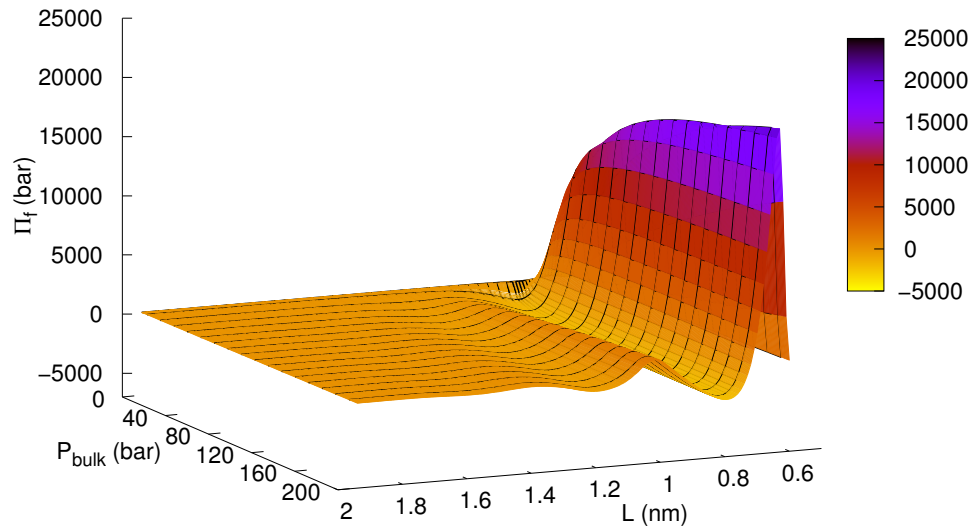
FIGURE 2 – Pore pressure as a function of bulk pressure and pore size at 373 K. Reproduced from [23].

The grand thermodynamic potential of a fluid confined in a slit-like pore of width L between two parallel plates of surface A_0 being [26] :

$$d\Omega = -SdT - \sum_i N_i d\mu_i + 2\gamma dA_0 - \Pi_f A_0 dL ,\qquad(3)$$

the pressure Π_f is :

$$\Pi_f = -\frac{1}{A_0}\left(\frac{\partial \Omega}{\partial L}\right)_{T,A_0,\mu_i} .\qquad(4)$$

Thus defined, Π_f becomes equal to the bulk pressure P_b when $L \to \infty$. It is the sum of two contributions $\Pi_f = P_b + f_s$, f_s being the solvation pressure as introduced by Hansen and McDonald [26] that vanishes when $L \to \infty$. One can demonstrate (see [23] for a complete development) from Eqs. (1) and (4) that, in case of a Steele-type external potential,we get :

$$\Pi_f = -\int_0^L \rho(z)\frac{\partial V^{\text{steele}}}{\partial z}(z)dz .\qquad(5)$$

Eq. (5) is in agreement with Eq. (6.5.5) of Hansen and McDonald's book [26] or [17]. Thus, the pressure inside a slit-like pore can be computed with Eq. (5) as soon as the density profiles have been computed with the NLDFT.

3   Results and discussion

The pore pressure Π_f has been computed in the whole range of micropores ($L < 2$ nm), for pressures up to 20 MPa at three temperatures : 303, 373 and 443 K. As an example, the 3D map of $\Pi_f = f(L, P_b)$ at 373 K is plotted in Fig. 2 whereas the 3D maps corresponding to the other temperatures are plotted in [23].

These maps $\Pi_f = f(L, P_b)$ clearly highlight that the pore pressure is a complex function of both pore size and thermodynamic conditions and that its variation is far from being obvious. Indeed, it depends on an intricate interplay between fluid-solid and fluid-fluid interactions ; the first ones being highly de-
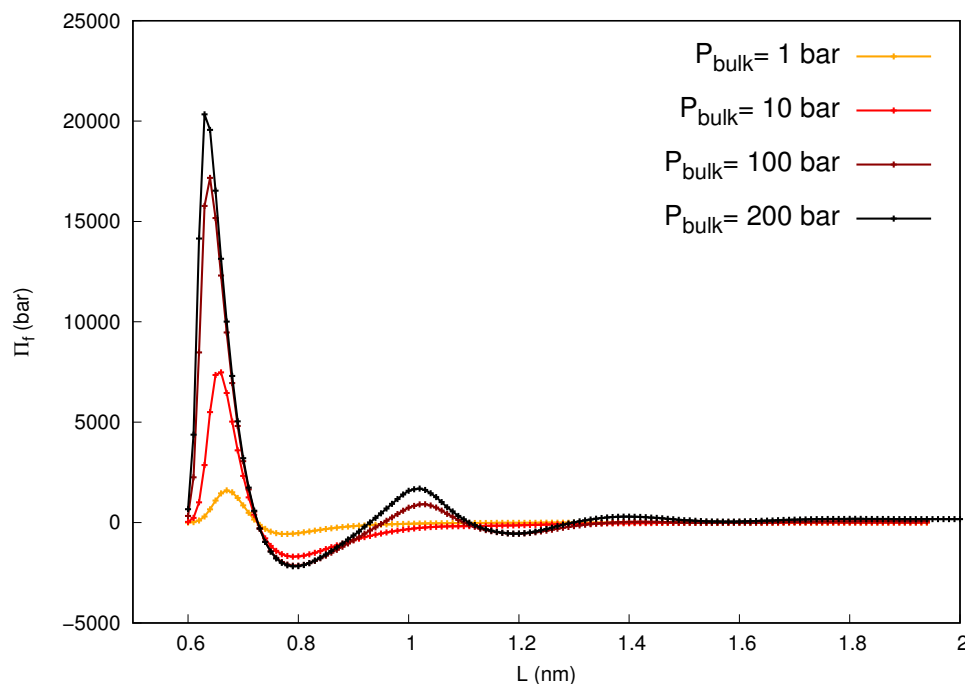
FIGURE 3 – Pore pressure evolution as a function of pore size for four different values of bulk pressure ($P_{\text{bulk}} \in \{1, 10, 100, 200\}$ bar) at 373 K. Reproduced from [23].

pendent on the distance between pore walls (given an adsorbent-adsorbate pair) and the latest ones on the thermodynamic conditions (pressure and temperature). As already observed in some molecular simulations [27, 28] and DFT [18, 22] calculations in idealised slit or cylindrical pores, the pore pressure oscillates as a function of pore width as a result of commensurate or incommensurate packing. As mentioned in the Introduction, this behaviour has already been presented in the literature with molecular simulations. However, the calculation speed of thermodynamic theories such as NLDFT compared to molecular simulations allows drawing complete maps of pore pressure for wide thermodynamic conditions and pore ranges. Pore pressures can reach extremely high values in the ultramicropores range. For the largest micropores, the difference between the pore and bulk pressures becomes negligible, the pores being filled with methane at a nearly *bulk* state, except for the layers on contact with the solid walls. Moreover, the pore pressure successively increases or decreases with bulk pressure depending on the considered pore width range.

As can be seen in Fig. 3, when L increases, the pore pressure exhibits an oscillatory decay similar to the one of the pair correlation function, giving successively repulsive or attractive force on the surface of the solid walls. Even if the oscillations of Π_f reflect the layers formation in the case of infinite parallel smooth walls, the same behavior has been observed in slit micropores of finite length [29] or of heterogeneous surface [22]. For the largest micropores ($L > 1.5$ nm), the packing effects become negligible and there is no more additional stress applied on the surfaces.

In order to have a better understanding of the relation between the pore density profiles and the induced attractive or repulsive pore pressure, it is useful to compute the work of the pore pressure as this latter allows to distinguish stable and unstable configurations, as shown in Fig. 4. Hence, it is demonstrated here that the pore pressure work can be used to identify unambiguously the pore widths that are commensurate (or non-commensurate) with the size of an adsorbent.
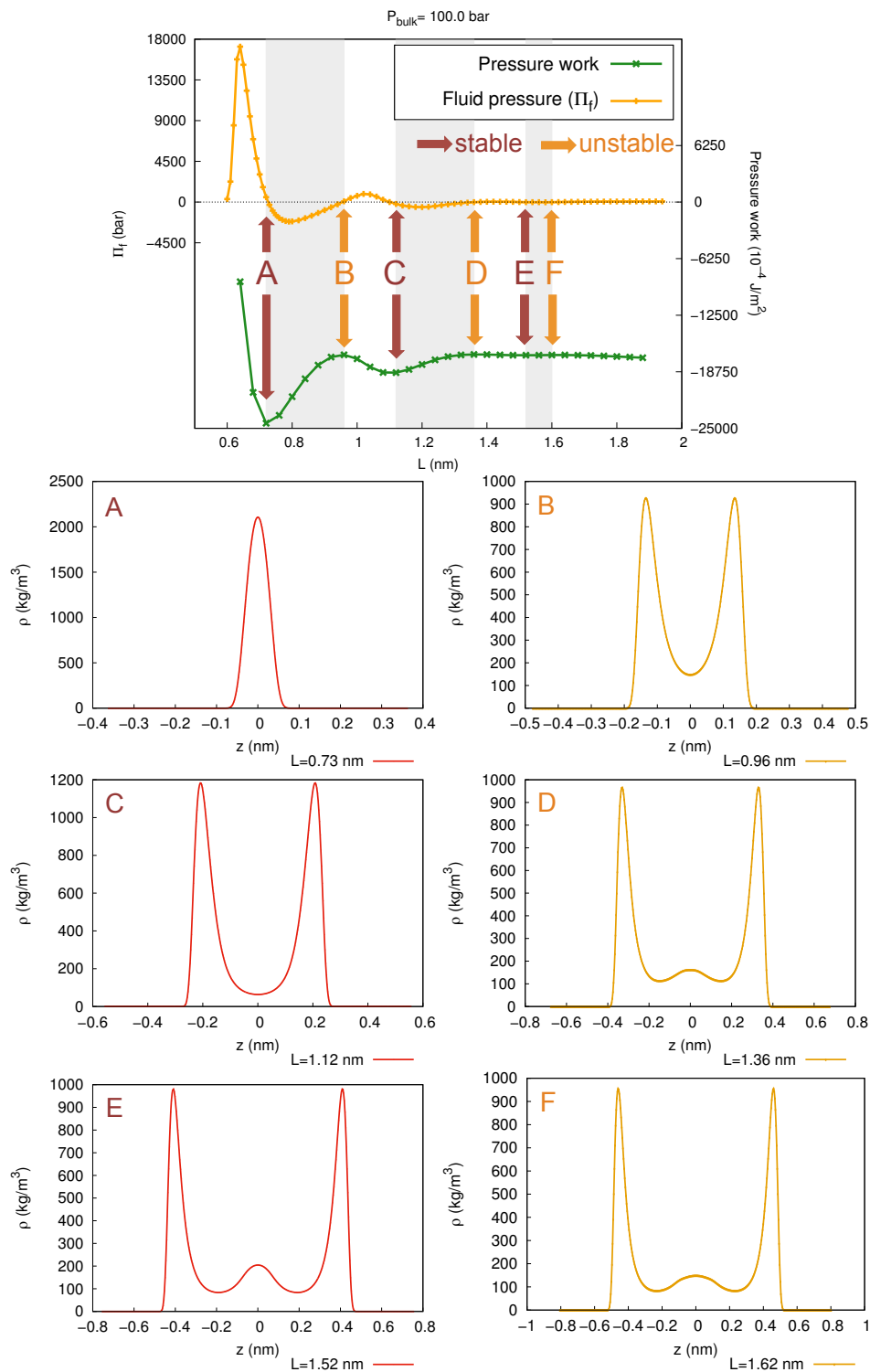
FIGURE 4 – Pore pressure work evolution as a function of pore widths (top) and characteristic pore density profiles (bottom, A to F) at 373 K. Reproduced from [23].

4 Concluding remarks

In this paper, we have shown that :

— A non-local density functional theory can be used to obtain highly resolved 3D maps of pore pressure *versus* pore widths and bulk pressure of methane in graphitic slit-shaped pores at different temperatures.

— These maps clearly highlight that, even for a non polar fluid such as methane, the pore pressure reaches very high values in the narrowest nanopores and is a complex function of both pore width and thermodynamic conditions.

— For ultramicropores accommodating only one fluid layer, the pores exhibit only positive pore pressure, and so positive adsorption stress causing expansion. For larger pores accommodating at least two overlapping layers, one can observe a transition from initial negative pore pressures to positive ones with increasing bulk pressures. This behaviour reflects the competition between fluid-solid interactions – predominant at low pressure – and fluid-fluid interactions – that dominate at higher pressure.

— For a given bulk pressure and with increasing pore widths, an oscillatory decay of the pore pressure is recovered giving successively repulsive or attractive force on the surface of the solids walls.

— This oscillatory decay reflects both the molecular packing and the fluid confinement. The pore pressure work distinguishes stable and unstable configurations. Therefore, it can be used to unambiguously identify the pore widths that are commensurate (or not-commensurate) with the size of an adsorbent.

These conclusions emphasise the need to have a reliable continuous thermodynamic model with a low computational cost to compute the pore fluid properties and their impact on the solid matrix in order to be coupled with a poromechanical model. A non-local DFT coupled with the SAFT equation-of-state can play this role for complex fluids on wide thermodynamic conditions.

Acknowledgements

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