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POROMECHANICS OF MICROPOROUS CARBONS: APPLICATION TO COAL SWELLING DURING CARBON STORAGE

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Introduction

Coal seams are naturally filled with natural gas. Enhanced Coal Bed Methane recovery (ECBM) is a technique which consists in injecting carbon dioxide (CO_2) in coal seams in order to enhance the recovery of the methane (CH_4) present in the coal seams. A major issue for the industrial development of this technique is the loss of permeability of the reservoirs during injection [1]. In a coal bed, most of the transport of fluids occurs in a network of natural fractures. The loss of permeability is attributed to the closure of the fractures induced by the swelling of the coal matrix during the progressive replacement of CH_4 by CO_2. Since both fluids are mostly adsorbed in the microporous matrix of coal, this particular problem raises the fundamental question of how adsorption impacts the mechanics of a microporous solid. In this work, we present a poromechanical modeling valid for microporous solids under adsorption and we apply this modeling to the specific case of ECBM. The first section presents the theoretical derivation of general constitutive equations of poromechanics which are valid for generic pore sizes and morphologies. In the second section, we apply this general poromechanics to the specific case of CH_4 adsorption in coal. We use molecular simulations to calibrate the derived constitutive laws. In the third section we validate this calibration by analyzing results of adsorption experiments in unjacketed conditions. The fourth section is dedicated to the case of CO_2 adsorption in coal. Finally in the last section, we use this modeling to predict the swelling of coal in the context of ECBM.

General constitutive equations of poromechanics

Usual poromechanics [2, 3] is valid for macroporous solids for which adsorption is negligible and all the fluid molecules in the pores are considered in their bulk state. For a poroelastic medium made of macropores, the constitutive equations of usual poromechanics relate the volumetric stress σ, deviatoric stresses s_{ij}, and fluid pore pressure P to the variation φ of porosity ($\varphi = \phi - \phi_0$, where ϕ is the actual porosity and ϕ_0 is the porosity in the state of reference), the volumetric strain ϵ and deviatoric strains e_{ij} of the medium:

$$\begin{aligned} \sigma &= K\epsilon - bP \\ \varphi &= b\epsilon + P/\overline{N} \\ s_{ij} &= 2\overline{G}e_{ij} \end{aligned} \tag{1}$$

where K, G, b, N are the bulk modulus, shear modulus, Biot coefficient, and Biot modulus of the medium, respectively. In a microporous solid, however, a large proportion of the fluid molecules may not be in their bulk state, but rather adsorbed in the micropores. For such a medium, the equations of usual poromechanics are not valid anymore and need to be extended. Extension to mesoporous solids, in which adsorption occurs at the surface of mesopores can be achieved by introducing interface effects [4]. Extension to microporous solids requires a more fundamental derivation since the notions of porosity or specific surface cannot be defined unambiguously in such media. In a recent work [5], we did such an extension to microporous solids.

We consider a porous solid in thermal equilibrium filled with a pure component fluid for which the bulk pressure is imposed by an external reservoir. The system is at fixed temperature T, strains ϵ and s_{ij}, and fluid chemical potential μ, while it can exchange heat and fluid molecules with its environment. The thermodynamic potential which is minimum at equilibrium is a hybrid potential ω_{hyb} per unit undeformed volume defined as:

$$\omega_{hyb} = \left(E - TS - \mu N\right)/V_0 \tag{2}$$

where E is the internal energy of the system, S is the entropy, N is the number of fluid molecules and V_0 is the undeformed volume of the medium. According to the definitions of the temperature ($T = \partial E/\partial S|_{\epsilon,e_{ij},N}$), of the chemical potential ($\mu = \partial E/\partial N|_{S,\epsilon,e_{ij}}$), and of the volumetric and deviatoric stresses ($\sigma = \partial f/\partial\epsilon|_{T,e_{ij},N}$ and $s_{ij} = \partial f/\partial e_{ij}|_{T,\epsilon,e_{i'j'\neq ij},N}$, where $f = \left(E - TS\right)/V_0$ is the Helmholtz free energy per unit undeformed volume), the energy balance associated to this hybrid thermodynamic potential is:

$$d\omega_{hyb} = \sigma d\epsilon + \sum_{i,j} s_{ij} de_{ij} - sdT - nd\mu \tag{3}$$

where $s = S/V_0$ and $n = N/V_0$. A general formulation of the constitutive equations of poromechanics can be obtained by integrating the following two Maxwell relations derived from the second derivatives of ω_{hyb}:

$$\left.\frac{\partial\sigma}{\partial\mu}\right|_{\epsilon,e_{ij},T} = -\left.\frac{\partial n}{\partial\epsilon}\right|_{e_{ij},T,\mu} \text{ and } \left.\frac{\partial s_{ij}}{\partial\mu}\right|_{\epsilon,e_{i'j'},T} = -\left.\frac{\partial n}{\partial e_{ij}}\right|_{\epsilon,e_{i'j'\neq ij},T,\mu} \tag{4}$$

For an isotropic medium that undergoes small strains, the amount n of fluid does not depend on the deviatoric strains e_{ij}. Integration with respect to the chemical potential of the fluid yields:

$$\begin{aligned} \sigma &= \sigma_0 - \frac{\partial}{\partial \epsilon}\left[\int_{-\infty}^{\mu} n d\mu\right]_{e_{ij},T,\mu} \\ n &= n(\epsilon,\mu) \\ s_{ij} &= (s_{ij})_0 \end{aligned} \quad (5)$$

where $\sigma_0 = \sigma(\mu \to -\infty)$ and $(s_{ij})_0 = s_{ij}(\mu \to -\infty)$ are the volumetric and deviatoric stresses that prevail when there is no fluid in the pores, respectively. For a linear elastic solid: $\sigma_0 = K\epsilon$ and $(s_{ij})_0 = 2Ge_{ij}$. Moreover, according to the Gibbs-Duhem equation in isothermal conditions ($d\mu = \overline{V}_b dP$, where $\overline{V}_b$ is the molar volume of the bulk fluid), the constitutive equations (5) can be rewritten:

$$\begin{aligned} \sigma &= K\epsilon - \frac{\partial}{\partial \epsilon}\left[\int_{0}^{P} n\overline{V}_b dP\right]_{e_{ij},T,P} \\ n\overline{V}_b &= n(\epsilon,P)\,\overline{V}_b(P) \\ s_{ij} &= 2Ge_{ij} \end{aligned} \quad (6)$$

According to this formulation of the constitutive equations, the stress of the porous solid can be fully determined as long as the amount n of fluid in the porous medium is known in function of both the chemical potential μ of the fluid and the volumetric strain ϵ. Equations (6) are a generalization of equations (1) valid whatever the size and morphology of the pores. Therefore, this new formulation is suitable to study the case of CH_4 and CO_2 adsorption in coal.

Case of CH_4 adsorption in coal

The extended state equations (6) can only be used if the adsorption isotherms $n(\epsilon,P)$ are known, which requires making the strain of the medium and the bulk pressure of the adsorbed fluid vary independently. Making those two parameters vary independently from each other cannot be done in a regular adsorption experiment in which the sample is immersed in a fluid. In such a case, the confining stress is equal to the opposite of the fluid pressure ($\sigma = -P$). As an alternative to laboratory experiments, we performed molecular simulations of CH_4 adsorption in a realistic molecular model of coal. This approach by molecular simulation enables easily to study adsorption in function of both strain and pressure and provides and interesting insight into the adsorption behavior in coal, complementary to laboratory experiments.

To simulate the microporous matrix of coal, we considered a molecular model of disordered microporous carbon obtained by hybrid reverse Monte Carlo reconstruction: the CS1000 model of Jain et al.[6]. To study the adsorption in function of the strain of the CS1000 skeleton, it is necessary to account for the flexibility of the skeleton and therefore to simulate the atom of the skeleton. The inter-atomic interactions within the CS1000 skeleton were modeled with modified Morse and harmonic potentials for the covalent bonds stretching and angle bending. Regarding the molecules of methane, we used Lennard-Jones potentials to model the interactions between the atoms of CS1000 and the methane molecules as well as between two methane molecules. The expressions of the potentials and the numerical values of the parameters are detailed in [5].

We performed Monte Carlo simulations to estimate the adsorbed amount in the CS1000 matrix. The simulations of adsorption were performed in the canonical ensemble regarding the atoms of the CS1000 sample and in the grand canonical ensemble regarding the molecules of methane. We considered various chemical potential of the fluid and various strain of the solid. Prior to the adsorption simulations, we applied the corresponding volumetric strain to the CS1000 matrix in absence of methane and let the atoms relax at each strain by performing a Monte Carlo simulation in the canonical ensemble. The final molecular configuration obtained at each strain was used as a starting configuration for the simulations of adsorption of methane. We display in Fig. 1 the adsorbed amount of methane per unit undeformed volume in function of the strain of the CS1000 sample for various bulk pressures of the methane. When the volumetric strain of the CS1000 sample was negative, the adsorbed amount of methane depended on the strain of the medium non-monotonically. In contrast, when the volumetric strain of the CS1000 was positive, the adsorbed amount of methane increased almost linearly with the strain of the medium.

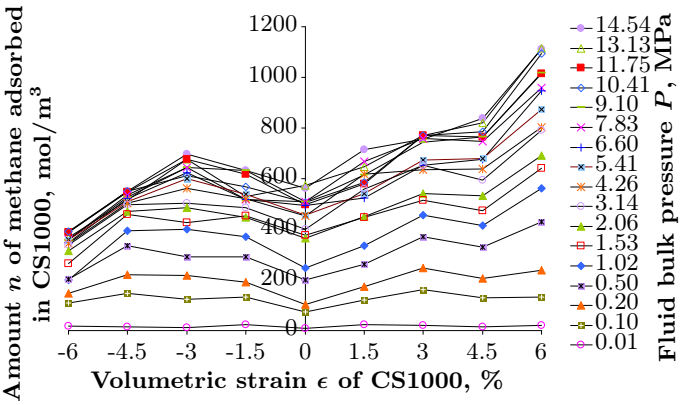


Fig. 1 Adsorbed amount of methane in CS1000 micropores per unit undeformed volume in function of both the fluid bulk pressure and the strain of the solid.

Such an observation suggests that, at least for cases in which coal swells, approximating the adsorption isotherm by its first-order expansion with respect to the strain of the porous medium should be reasonable:

$$n(\epsilon,P) = n^0.(1 + C(P)\,\epsilon) \quad (7)$$

where $n^0 = n(\epsilon = 0)$ is the amount of fluid adsorbed at zero strain. We calculated the average of the derivative $\partial n/\partial \epsilon|_P$ over all positive strains and compared this average to the amount n^0 of fluid adsorbed at zero strain. The result of the comparison is displayed in Fig. 2. The

comparison shows that the two quantities were almost proportional to each other, which means that the coupling coefficient $C(P)$ in Eq. (7) did almost not depend on the pressure P of the fluid: $C_{\mathrm{CH_4}}(P) \approx 6.30 \pm 15\%$ on the whole range of pressures considered. Using the first-order expansion (7) of the adsorption isotherm the first poromechanical constitutive equation (6) can be simplified.

$$\sigma = K\epsilon - C\int_0^P n^0 \overline{V}_b dP \tag{8}$$

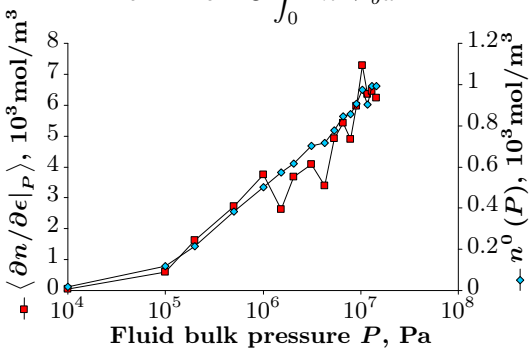


Fig. 2 Adsorption isotherm at zero strain and derivative of the adsorbed amount with respect to the strain.

The linearized constitutive equation (8) is a significant simplification since one has to know how adsorption depends on the pressure of the fluid only. For positive adsorption ($n^0 > 0$), Eq. (8) predicts a swelling of the porous medium ($\Delta\epsilon > 0$) when the confining stress σ is maintained at a constant value, or, conversely, a compression of the medium ($\Delta\sigma < 0$) when the strain ϵ is constant. This behavior seems consistent with the phenomenon of coal swelling.

Validation with laboratory experiments

A partial validation of our results with experiments is possible: we considered the experimental results of Ottiger et al. [7] who immersed coal samples in methane and measured the total amount of fluid adsorbed in the sample and the swelling of the sample. In such an experiment, the porous solid is in unjacketed conditions: the volumetric stress σ is equal to the opposite $-P$ of the fluid bulk pressure. The strain ϵ^u and the amount n^u of fluid adsorbed both depend on the fluid bulk pressure only. The first constitutive equation (6) yields a relation that the volumetric strain $\epsilon^u(P)$ must verify:

$$-P = K\epsilon^u(P) - \frac{\partial}{\partial\epsilon}\left[\int_0^P n(\epsilon, P)\,\overline{V}_b dP\right]_{\epsilon=\epsilon^u} \tag{9}$$

Assuming that the adsorption isotherm can be well approximated by its first-order expansion with respect to the strain (Eq. 7) , a differentiation of Eq. (9) with respect to the pressure P of the fluid yields:

$$C(P) = \frac{1 + Kd\epsilon^u/dP}{n^u\overline{V}_b - \epsilon^u(1 + Kd\epsilon^u/dP)} \tag{10}$$

Using this equation, the coupling coefficient $C(P)$ can be fully determined from an immersion experiment in which both the adsorption isotherm $n^u(P)$ and the volumetric strain $\epsilon^u(P)$ are measured. Based on the results reported by Ottiger et al. [7] and assuming a coal density of 1300 kg/m^3, we calculated the coupling coefficient $C(P)$ with Eq. (10). We display in Fig. 3 the coupling coefficient $C_{\mathrm{CH_4}}(P)$ calculated for methane adsorption for bulk moduli K ranging from 1 GPa to 4 GPa, which is the range of values usually observed for coal. The back-calculated coupling coefficient was the least pressure-dependent for a bulk modulus $K = 2.65$ GPa. For such a bulk modulus, we back-calculated a coupling coefficient $C_{\mathrm{CH_4}}(P) = 6.05 \pm 7\%$, i.e., a coupling coefficient $C_{\mathrm{CH_4}}(P)$ which hardly depended on the bulk fluid pressure. The coupling coefficient $C_{\mathrm{CH_4}} = 6.05$ back-calculated from the experimental data of Ottiger et al. compares very well with the coupling coefficient $C_{\mathrm{CH_4}} = 6.30$ obtained from molecular simulations. This comparison brings confidence in the results of the molecular simulations and therefore validates the use of the poroelastic constitutive equation (8) to describe the poromechanical behavior of coal saturated with methane.

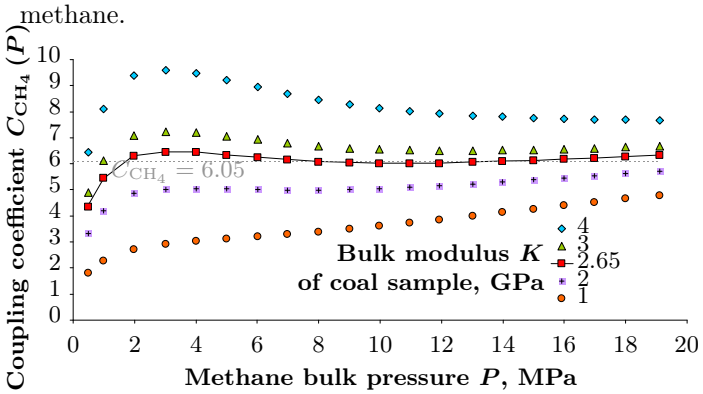


Fig. 3 Coupling coefficient $C_{\mathrm{CH_4}}(P)$ for the adsorption of methane in coal estimated from the immersion experiments of Ottiger et al. [7].

Case of CO_2 adsorption in coal

As we did for methane, we back-calculated the coupling coefficient $C_{\mathrm{CO_2}}(P)$ for carbon dioxide from the immersion experiments of Ottiger et al. [7]. The results of this calculation are displayed in Fig. 4. For fluid bulk pressures lower than 8 MPa, the values of $C_{\mathrm{CO_2}}(P)$ calculated for a bulk modulus of 2.65 GPa hardly depended on the fluid pressure and were very similar to the values obtained for methane: $C_{\mathrm{CO_2}}(P < 8\ \mathrm{MPa}) = 6.40 \pm 7\%$. But for pressures larger than 8 MPa, the coupling coefficient $C_{\mathrm{CO_2}}(P)$ became pressure dependent and reached a maximum value: $C_{\mathrm{CO_2}}(P = 10.76\ \mathrm{MPa}) = 10.53$.

The fluid pressure at which the coupling coefficient $C_{\mathrm{CO_2}}(P)$ increased sharply is close to the critical pressure of CO_2. The specificity of supercritical carbon dioxide around this pressure is that significant fluctuations of density are observed at the molecular scale: clusters of a few molecules large form. The size of these clusters can

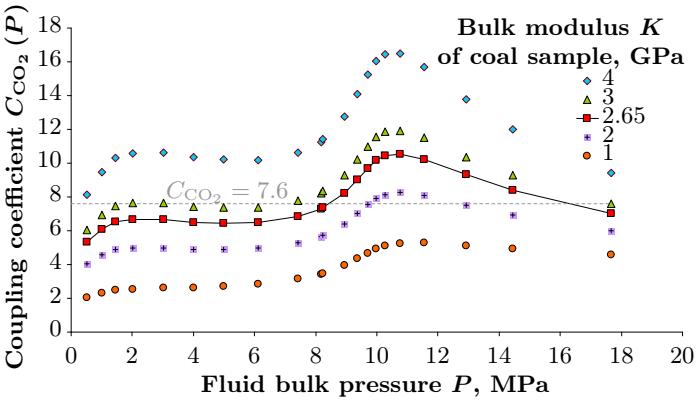


Fig. 4 Coupling coefficient $C_{\mathrm{CO_2}}(P)$ for the adsorption of carbon dioxide in coal estimated from the immersion experiments of Ottiger et al.[7].

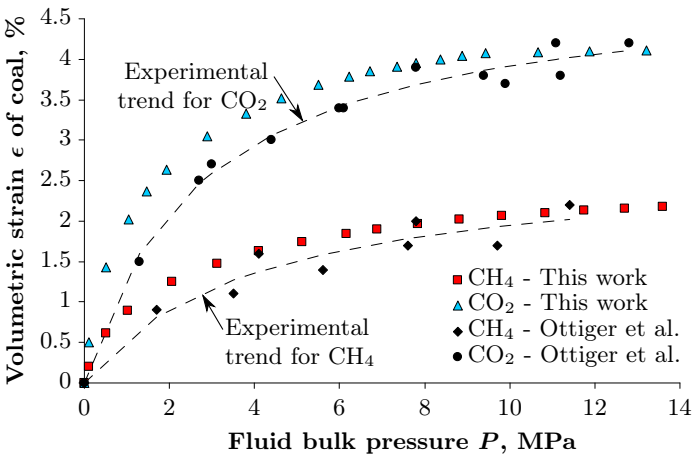


Fig. 5 Swelling of a coal sample immersed in pure CO_2 and pure CH_4, measured experimentally and estimated with the poromechanical model.

be estimated from scattering experiments [8]: the maximum size of the clusters for the temperature considered in the experiments of Ottiger et al. (318.15 K) is about 10 Å at $P = 10$ MPa, which corresponds to a cluster of 5 or 6 molecules. The aggregation of carbon dioxide molecules is responsible for the multilayer adsorption of carbon dioxide in mesopores of coal [4]. We interpret the pressure dependence of the coupling coefficient $C_{\mathrm{CO_2}}(P)$ (Fig. 4) as due to aggregation of carbon dioxide which increases significantly the adsorption in micropores larger than $10-15$ Å and in mesopores.

As a rough modeling, in what follows, we considered that the linearized constitutive equations (8) remain valid to describe the poromechanical behavior of coal saturated with CO_2, in which the coupling coefficient $C_{\mathrm{CO_2}}(P)$ is assumed independent of the pressure. We chose the value $C_{\mathrm{CO_2}} = 7.60$, which is an average value over the range of fluid pressures considered in this study.

Application to estimate coal swelling

By using Eq. (8) and the coupling cofficients $C_{\mathrm{CH_4}}$ and $C_{\mathrm{CO_2}}$ obtained in the two previous sections combined with adsorption isotherms $n^0(P)$, we can estimate the mechanical behavior of coal filled with pure CO_2 and pure CH_4. We display in Fig. 5 the swelling we could estimate for coal sample immersed in pure CO_2 and pure CH_4 together with the measurements performed by Ottiger et al. [7]. For our estimation, we used adsorption isotherms $n^0(P)$ obtained by molecular simulation of adsorption of CO_2 and CH_4 in the CS1000 matrix considered rigid (the molecular interactions for CO_2 are detailed in [4]). The swelling we estimated is consistent with the experiments. At pressures lower than 2 MPa, the swelling was overestimated for both fluids because the coupling coefficients $C_{\mathrm{CH_4}}$ and $C_{\mathrm{CO_2}}$ overestimate the actual coupling coefficients in this range of pressure (see Figs. 3 and 4). At larger fluid pressures, because of the integral form of Eq. (8), the initial overestimation is propagated but the estimation and the experimental results followed very similar evolutions.

Conclusion

In this work, we developed a comprehensive approach to account for the effect of adsorption on the mechanics of microporous solids. The derived constitutive equations were calibrated for the specific case of CO_2 and CH_4 adsorption in coal. The application of the proposed modeling to ECBM requires to further extend the constitutive equation (8) to mixture adsorption. In a recent work [9], we presented such an extension and we used this modeling to estimate the differential swelling of coal during ECBM operations at different geological depths. The approach we presented is not limited to the specific case of coal, but could be adapted to a wider range of microporous solids. In particular, the linear dependency between adsorption and strain appears to be characteristic of disordered microporous solids [5] and may apply to disordered porous carbons in general, as long as the fluid considered does not exhibit phase change.

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