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**₁ A transverse isotropic model for microporous solids -
₂ Application to coal matrix adsorption and swelling**

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3 **Abstract.** Understanding the adsorption-induced swelling in coal is crit-
4 ical for predictable and enhanced coal bed methane production. The coal ma-
5 trix is a natural anisotropic disordered microporous solid. We develop an elas-
6 tic transverse isotropic poromechanical model for microporous solids which
7 couples adsorption and strain through adsorption stress functions, and ex-
8 presses the adsorption isotherm as a multivariate function depending on fluid
9 pressure and solid strains. Experimental data from the literature help invert-
10 ing the anisotropic adsorptive-mechanical properties of Brzeszcze coal sam-
11 ples exposed to CO₂. Main findings include: (1) adsorption-induced swelling
12 can be modeled by including fluid-specific and pressure-dependent adsorp-
13 tion stress functions into equilibrium equations, (2) modeling results suggest
14 that swelling anisotropy is mostly caused by anisotropy of the solid mechan-
15 ical properties, and (3) the total amount of adsorbed gas measured by im-
16 mersing coal in the adsorbate overestimates adsorption amount compared
17 to in-situ conditions up to ~20%. The developed fully coupled model can
18 be upscaled to determine the coal seam permeability through permeability-
19 stress relationships.

1. Introduction

20 The understanding of adsorption of gases in mesoporous and microporous solids is im-
21 portant for applications in gas capture, gas separation, and gas desorption/adsorption in
22 sedimentary rocks. Micropores are defined by the IUPAC as pores with width not exceed-
23 ing 2 nm. We consider here a broader definition of microporous solids including porous
24 solids with pores sized in the order of a few nanometers. Natural microporous solids in-
25 clude coal, kerogen, zeolites, and gas hydrates; while artificial microporous solids include
26 microcarbon and metal organic frameworks among others [*Ravikovitch and Neimark, 2006;*
27 *Mazumder et al., 2006; Vandembroucke and Largeau, 2007; Sloan and Koh, 2008; Kowal-*
28 *czyk et al., 2008; Neimark et al., 2011*]. From another point of view, microporous solids
29 can be classified as regards their structure in crystalline (ordered structure: metal organic
30 frameworks, zeolites, hydrates) or disordered (coal, kerogen, microporous carbon). Nano-
31 sized micropores can host just a few fluid molecules. The adsorption of fluids in these
32 pores can lead to their expansion or contraction depending on the pore size, geometry,
33 and fluid-solid interaction [*Kowalczyk et al., 2008; Pijaudier-Cabot et al., 2011; Brochard*
34 *et al., 2012*]. Macroscopically, adsorption-driven changes of pore size or pressure upscale
35 as strains (or stresses if strains are prescribed).

36 This coupling between strain and adsorption is particularly important in the context of
37 underground adsorptive geomaterials, such as coal and organic shales [*Busch et al., 2008;*
38 *Weniger et al., 2010*]. Hydrocarbon production from these reservoirs imposes significant
39 changes in stresses coupled with adsorption or desorption leading to strains which affect
40 the aperture and permeability of natural and generated fractures. The adsorption-strain

41 coupling is critical to defining production rates of natural gas from highly-adsorptive coal
42 bed seams [*Palmer and Mansoori, 1998; Pan and Connell, 2012*].

43 The adsorption and swelling of various gases including carbon dioxide CO₂, methane
44 CH₄, and nitrogen N₂ in coal has been largely studied in the past decades [*Reucroft and*
45 *Sethuraman, 1987; Ceglarska-Stefanska and Czaplinski, 1993; Levine, 1996; Ceglarska-*
46 *Stefanska and Zarebska, 2002; Mazumder et al., 2006; Pini et al., 2009*]. Adsorbed amounts
47 are usually measured in the laboratory in terms of excess adsorbed amount, that is, the
48 amount of fluid in excess of the amount of fluid which would occupy the pore volume
49 in bulk conditions. In general for low-medium gas pressure, up to ~ 10 MPa, the rule
50 “the greater the pressure, the greater the total adsorbed amount” is valid. In this range,
51 coal swelling is usually proportional to the amount of adsorbed gas. For higher pressures,
52 the bulk fluid pressure compresses the solid skeleton and may prevail over adsorption-
53 induced swelling [*Moffat and Weale, 1954; Pan and Connell, 2007; Hol and Spiers, 2012*].
54 In fact, recent studies show that the application of compressive confining stresses (and
55 ensuing strains) to coal swollen and equilibrated with CO₂ at a certain pressure induce the
56 expulsion of adsorbed gas [*Hol et al., 2011, 2012*]. This desorption induced by mechanical
57 stresses is not due to the loss of pore accessibility caused by permeability reduction upon
58 the application of compressive external stresses, phenomenon which is also observed in
59 coal [*Pone et al., 2009; Wang et al., 2011*].

60 Such a particular behavior of coal motivated the extension of the theory of porome-
61 chanics to include adsorption phenomena in microporous solids. *Brochard et al.* [2012]
62 proposed a set of poromechanical equations valid for linear elastic isotropic microporous
63 solids which considers as main variable the total amount of adsorbed fluid as a function

64 of fluid pressure and solid strain, without a need for introducing the notion of pore vol-
65 ume. The model is based on first principles, shows good swelling prediction capability,
66 and eventually leads to the classical theory of poromechanics if adsorption is negligible.

67 Although *Brochard et al.* [2012] developed a model applicable to isotropic coal matrix,
68 most sedimentary geomaterials are not isotropic. Vertical deposition and overburden at
69 zero-lateral strain favor transverse isotropic symmetry [*Thomsen*, 1986; *Johnston and*
70 *Christensen*, 1995; *Vernik and Nur*, 1992]. Anisotropic poromechanical responses can be
71 quantified by the Biot effective stress coefficient tensor or equivalently by the Skempton
72 tensor [*Cheng*, 1997; *Cowin*, 2004]. The mechanical and swelling properties of coal are
73 notably anisotropic, with a major influence of the orientation respect to the bedding plane
74 and the proximity to cleats [*Cody et al.*, 1988; *Levine*, 1996; *Hol and Spiers*, 2012; *Day*
75 *et al.*, 2010; *Morcote et al.*, 2010].

76 This article presents an extension of the poromechanical model for adsorptive microp-
77 orous solids developed by *Brochard et al.* [2012] to take into account material properties
78 anisotropy. The anisotropy is integrated for both adsorption-induced phenomena and
79 mechanical properties, and it is implemented by means of a transverse isotropic model
80 pertinent to sedimentary rocks. The model is used to invert the anisotropic adsorptive-
81 mechanical properties of a sample of Brzeszcze coal tested by *Hol and Spiers* [2012]. The
82 model offers further insight into the relationship between swelling and adsorption.

2. Model formulation

83 The model is based on energy conservation and follows from a thermodynamical formu-
84 lation. A more detailed formulation developed for isotropic microporous solids is available
85 elsewhere [*Brochard et al.*, 2012]. We aim at developing the poromechanical equations for

86 adsorbing microporous solids which exhibit transverse isotropic properties. The interested
 87 reader will find similar theoretical developments applied to various poromechanical prob-
 88 lems in [Coussy, 2004, 2010]. The theory of poroelasticity for anisotropic macroporous
 89 solids has been revisited by several authors [Cheng, 1997; Coussy, 2004; Cowin, 2004].

2.1. Energy conservation

90 Consider a representative elementary volume of a microporous solid with free energy per
 91 unit volume f [J/L], subjected to stresses σ_{ij} [Pa], and whose adsorbed fluid has a molar
 92 chemical potential μ [J/mol]. Energy conservation under isothermal conditions dictates

$$df = \sum_{i,j} \sigma_{ij} d\varepsilon_{ij} + \mu dn \quad (1)$$

93 being ε_{ij} the strain tensor [-], and n the number of moles of fluid per unit volume of
 94 undeformed microporous solid [mol/L]. Strains are calculated respect to the original con-
 95 figuration (Lagrangian formulation). By changing variables, the following holds

$$d(f - n\mu) = \sum_{i,j} \sigma_{ij} d\varepsilon_{ij} - nd\mu \quad (2)$$

96 The first term to the right of the equality represents the incremental work done by
 97 stresses and the second represents the change of energy associated to changes in the
 98 chemical potential of the fluid phase. The development of the model consists in finding
 99 expressions to the variables σ_{ij} , and n as a function of the other variables. Volume
 100 average considerations, Maxwell's relations, and the Gibbs-Duhem equation are used to
 101 this purpose.

2.2. Derivation of equations of state

Let us apply Maxwell's relation on the previous energy conservation equality (Eq. 2),

$$\frac{\partial^2(f - n\mu)}{\partial \varepsilon_{ij} \partial \mu} = \frac{\partial^2(f - n\mu)}{\partial \mu \partial \varepsilon_{ij}} \quad (3)$$

Derivation leads to

$$\left. \frac{\partial \sigma_{ij}}{\partial \mu} \right|_{\varepsilon_{kl \neq ij}} = - \left. \frac{\partial n}{\partial \varepsilon_{ij}} \right|_{\mu, \varepsilon_{kl \neq ij}} \quad (4)$$

The equality holds for strains $\varepsilon_{kl \neq ij}$ constant. By integrating this equation on the molar chemical potential μ we obtain the following equation

$$\sigma_{ij} = \Psi_{ij}(\underline{\varepsilon}) - \int_{-\infty}^{\mu} \left. \frac{\partial n}{\partial \varepsilon_{ij}} \right|_{\mu, \varepsilon_{kl \neq ij}} d\mu \quad (5)$$

where Ψ_{ij} results from this integration and, thus, is a function independent from the fluid chemical potential μ . The molar chemical potential μ can be re-written using Gibbs-Duhem relation for isothermal conditions $d\mu = \bar{V}_b(p)dp$, where \bar{V}_b is the molar volume of the fluid in bulk conditions [L/mol] as a function of temperature and pressure, and p is the thermodynamic pressure of the fluid [Pa] defined as the pressure of the bulk fluid at the same chemical potential as the adsorbed phase. Hence, Eq. (5) can be written as follows

$$\sigma_{ij} = \Psi_{ij}(\underline{\varepsilon}) - \int_0^p \left. \frac{\partial n}{\partial \varepsilon_{ij}} \right|_{p, \varepsilon_{kl \neq ij}} \bar{V}_b(p) dp \quad (6)$$

The first term to the right of the equality Ψ_{ij} represents the “dry” response of the specimen to strains (without the fluid phase) and the integral term represents the response

115 to fluid loading as a function of fluid pressure and solid strain. For example, assuming
 116 linear elasticity, isotropic material properties, and that the fluid is in bulk conditions,
 117 *Brochard et al.* [2012] show that Eq. (6) permits recovering the classical equations of
 118 poroelasticity $\sigma = K\epsilon - bp$, where K is the drained bulk modulus, ϵ is the volumetric
 119 strain, and b is the Biot coefficient).

2.3. Simplification for transverse isotropic coal

120 **Linear elastic transverse isotropy.** The functions Ψ_{ij} depend on strains $\underline{\underline{\epsilon}}$ only, hence,
 121 any linear or non-linear elastic constitutive law may be used. We use transverse isotropic
 122 linear elasticity for functions Ψ_{ij} in this formulation. Transverse isotropic materials are
 123 defined by an axis of symmetry in their elastic properties (say axis 3 in this development).
 124 The reduced stiffness matrix in Voigt notation C_{ij} has 5 independent constants. Thus,
 125 the “dry” response of a generic transversely isotropic porous solid $\sigma_{ij} = \Psi_{ij}(\underline{\underline{\epsilon}})$ is

$$\begin{cases} \sigma_{11} = C_{11}\epsilon_{11} + C_{12}\epsilon_{22} + C_{13}\epsilon_{33} \\ \sigma_{22} = C_{12}\epsilon_{11} + C_{11}\epsilon_{22} + C_{13}\epsilon_{33} \\ \sigma_{33} = C_{13}\epsilon_{11} + C_{13}\epsilon_{22} + C_{33}\epsilon_{33} \\ \sigma_{23} = 2C_{44}\epsilon_{23} \\ \sigma_{31} = 2C_{44}\epsilon_{31} \\ \sigma_{12} = (C_{11} - C_{12})\epsilon_{12} \end{cases} \quad (7)$$

126 Deformation can be expressed in terms of engineering elastic constants E (Young mod-
 127 ulus in direction 1 and 2), E_3 (Young modulus in direction 3), ν (Poisson ratio in plane
 128 1-2), ν_3 (Poisson ratio in planes 1-3 and 2-3), and G_3 (shear modulus in plane 1-3 and
 129 2-3) as $\epsilon_{kl} = \Psi'_{kl}(\underline{\underline{\sigma}})$,

$$\left\{ \begin{array}{l} \varepsilon_{11} = (1/E)\sigma_{11} - (\nu/E)\sigma_{22} - (\nu_3/E_3)\sigma_{33} \\ \varepsilon_{22} = -(\nu/E)\sigma_{11} + (1/E)\sigma_{22} - (\nu_3/E_3)\sigma_{33} \\ \varepsilon_{33} = -(\nu_3/E_3)\sigma_{11} - (\nu_3/E_3)\sigma_{22} + (1/E_3)\sigma_{33} \\ 2\varepsilon_{23} = (1/G_3)\sigma_{23} \\ 2\varepsilon_{31} = (1/G_3)\sigma_{31} \\ 2\varepsilon_{12} = [2(1 + \nu)/E]\sigma_{12} \end{array} \right. \quad (8)$$

130 **Multivariate adsorption isotherm.** The derivative $\partial n / \partial \varepsilon_{ij} \big|_{p, \varepsilon_{kl} \neq ij}$ in the right hand
131 side of Eq. (6) can be further developed if the total amount of adsorbed fluid $n(p, \varepsilon_{ij})$ is
132 known as a function of the thermodynamic pressure of the fluid p and the strains of the
133 microporous solid ε_{ij} . Considering small strains, this multivariate adsorption isotherm
134 can be expressed as a first-order expansion with respect to strains, such that,

$$n(p, \varepsilon_{ij}) = n_0(p)[1 + c_1(p)\varepsilon_{11} + c_2(p)\varepsilon_{22} + c_3(p)\varepsilon_{33}] \quad (9)$$

135 where $n_0(p) = n(p, \underline{0})$ is the total amount of adsorbed fluid at zero solid strain, and $c_1(p)$,
136 $c_2(p)$, $c_3(p)$ are the adsorption-strain coupling functions for each direction [-]. Coefficients
137 $c_i(p)$ capture the coupling between adsorption and strain, and depend on fluid pressure,
138 type of gas, pore shape and size distribution. *Brochard et al.* [2012] performed molecular
139 simulations of CH₄ adsorption in disordered organic microporous solids and validated this
140 first-order expansion (Eq. 9) in the isotropic case, for volumetric strains up to $\sim 10\%$. Such
141 strains are sufficiently large to consider that this first-order expansion is valid for coal in
142 practical conditions. We will consider that this validity remains in the case of transverse
143 isotropy. Also, *Brochard et al.* [2012] show that adsorption-strain coupling coefficients can
144 be negative when adsorption induces pore shrinkage or positive if pore expansion prevails.
145 Transverse isotropy in the adsorption-strain coupling imposes $c_1(p) = c_2(p)$.

146 Various adsorbing materials, including coal exposed at moderate gas pressure, are well
 147 described by Langmuir adsorption isotherms as a function of pressure or more appropri-
 148 ately as a function of the fluid fugacity [*Fowler*, 1935; *Vandamme et. al.*, 2010; *Hol et al.*,
 149 2011]. Hence, assuming a Langmuir-type of adsorption as a function of pressure for the
 150 undeformed microporous coal leads to

$$n_0(p) = n_0^{max} \frac{p}{\beta + p} \quad (10)$$

151 with n_0^{max} being the maximum total amount of adsorbed fluid at zero solid strain [mol/L],
 152 and β the Langmuir pressure [Pa] at which one half of the adsorption capacity is reached
 153 while keeping zero solid strain.

154 From Eq. (9) and (10), the derivatives of $n(p, \varepsilon_{ij})$ with respect to strains ε_{ij} result:

$$\left. \frac{\partial n}{\partial \varepsilon_{ij}} \right|_{p, \varepsilon_{kl} \neq ij} = c_i(p) n_0(p) \delta_{ij} \quad (11)$$

155 Eq. (9) implicitly assumes that the principal directions of the tensor $\partial n / \partial \varepsilon_{ij} |_{p, \varepsilon_{kl} \neq ij}$ co-
 156 incide with the geometrical axes of symmetry. Hence, these derivatives are non-zero only
 157 with respect to strain components ε_{ii} and vanish for shear strains components ε_{ij} with
 158 $i \neq j$. Back to Eq. (6), adsorption-induced strains and stresses on the anisotropic micro-
 159 porous solid can be quantified with terms named $s_i^a(p) = \int_0^p \partial n / \partial \varepsilon_{ij} |_{p, \varepsilon_{kl} \neq ij} \bar{V}_b dp$, which,
 160 with the help of Eq. (11), become

$$s_i^a(p) = \int_0^p c_i(p) n_0(p) \bar{V}_b(p) dp \quad (12)$$

161 We call these terms “adsorption stresses” as motivated by an analogy with the theory
 162 formulated by *Ravikovitch and Neimark* [2006]. Physically, these terms quantify the
 163 stresses needed to keep the microporous solid at zero volumetric strain during adsorption.

164 **Final equations.** Combining the linear elastic constitutive equations (Eq. 7) with
 165 adsorption stresses (Eq. 12), the set of equations (Eq. 6) becomes

$$\left\{ \begin{array}{l} \sigma_{11} = C_{11}\varepsilon_{11} + C_{12}\varepsilon_{22} + C_{13}\varepsilon_{33} - s_1^a(p) \\ \sigma_{22} = C_{12}\varepsilon_{11} + C_{11}\varepsilon_{22} + C_{13}\varepsilon_{33} - s_1^a(p) \\ \sigma_{33} = C_{13}\varepsilon_{11} + C_{13}\varepsilon_{22} + C_{33}\varepsilon_{33} - s_3^a(p) \\ \sigma_{23} = 2C_{44}\varepsilon_{23} \\ \sigma_{31} = 2C_{44}\varepsilon_{31} \\ \sigma_{12} = (C_{11} - C_{12})\varepsilon_{12} \end{array} \right. \quad (13)$$

166 The model relies on five mechanical parameters C_{11} , C_{33} , C_{12} , C_{13} , C_{44} (stiffness co-
 167 efficients which can be expressed as a function of E , ν , E_3 , ν_3 , G_3), one fluid equation
 168 of state $\bar{V}_b(p)$ at a given temperature, two characteristic total adsorption parameters
 169 n_0^{max} and β for the microporous solid at zero strain, and two adsorption-strain coupling
 170 pressure-dependent functions $c_1(p)$ and $c_3(p)$.

3. Application example - Unconstrained coal swelling

171 Let us consider a piece of coal matrix immersed in CO_2 under unconstrained dis-
 172 placement boundary conditions (unjacketed: no membrane or wall, the solid is free
 173 to swell), such that CO_2 pressure applies isotropic loading and no shear on the solid
 174 ($\sigma_{11} = \sigma_{22} = \sigma_{33} = -p$; $\sigma_{ij} = 0$ for $i \neq j$). The coal is in thermodynamical equilibrium,
 175 thus, the chemical potential of the bulk fluid at pressure p is the same as the chemical
 176 potential of the adsorbed fluid. Isotropic loading in a transverse isotropic medium imposes
 177 $\varepsilon_{11} = \varepsilon_{22}$ in the general case $C_{11} \neq C_{12}$ (from Eq. 13), $\varepsilon_{11} = \varepsilon_{22} = \varepsilon_1$ the principal strain

178 on the bedding plane, and $\varepsilon_{33} = \varepsilon_3$ the principal strain perpendicular to the bedding
 179 plane, hence, Eq. (13) reduces to

$$\begin{cases} \sigma_{11} = \sigma_{22} = -p = (C_{11} + C_{12})\varepsilon_1 + C_{13}\varepsilon_3 - s_1^a(p) \\ \sigma_{33} = -p = 2C_{13}\varepsilon_1 + C_{33}\varepsilon_3 - s_3^a(p) \end{cases} \quad (14)$$

180 Let us write the principal strains ε_1 and ε_3 as function of stresses using the engineering
 181 elastic constants. Swelling strains result

$$\begin{bmatrix} \varepsilon_1 \\ \varepsilon_3 \end{bmatrix} = \begin{bmatrix} \frac{1-\nu}{E} & -\frac{\nu_3}{E_3} \\ -2\frac{\nu_3}{E_3} & \frac{1}{E_3} \end{bmatrix} \begin{bmatrix} s_1^a(p) - p \\ s_3^a(p) - p \end{bmatrix} \quad (15)$$

182 Recent experimental results show the swelling of cylindrical Brzeszcze coal specimens
 183 immersed in CO₂ up to 100 MPa of fluid pressure (specimen size 4mm length and 4mm
 184 diameter [*Hol and Spiers, 2012*]). Strains are measured in two perpendicular directions in
 185 the bedding plane (noted ε_x and ε_y), at 45° between the x and y axes, and perpendicular to
 186 the bedding plane (this latter noted ε_z). Results show a clear orthotropic swelling of coal
 187 specimens, being the strain perpendicular to the bedding plane the highest $\varepsilon_z > \varepsilon_y \sim \varepsilon_x$.
 188 We consider the major principal strain $\varepsilon_3 = \varepsilon_z$. We calculate the other two principal
 189 strains from the original data set based on the three strains measured in the bedding plane.
 190 Figures 1-a and 1-d show the principal strains for two coal specimens 364-1 and 364-2,
 191 as named in the source reference. Although the experimental results show an orthotropic
 192 response, we fit a transverse isotropic model in views of upscaling to coal seams with
 193 transverse isotropic properties and to reduce the number of inverted parameters. The
 194 experimental principal strain ε_3 and the mean of the experimental principal strains on
 195 the bedding plane $(\varepsilon_1 + \varepsilon_2)/2$ are used to validate the transverse isotropic model.

196 Additional data help us invert the coal adsorptive-mechanical properties; these data
 197 include: (1) total amount of adsorption in Brzeszcze coal immersed in CO₂ up to 15 MPa
 198 (estimated from excess adsorbed amount measurements at 45°C by *Gensterblum et al.*
 199 [2010] with best fitting adsorbed phase volume per unit mass of coal $V_{ads}/m_{coal} = 0.055$
 200 cm³/g - see Auxiliary Material); (2) the dry coal mass density $\rho \sim 1343$ kg/m³ [*Hol et al.*,
 201 2011]; (3) the molar volume of CO₂ at 40°C as a function of pressure (from equation of
 202 state by *Span and Wagner* [1996]). The coal is expected to adsorb slightly less CO₂ at
 203 45°C than at 40°C, temperature at which swelling strains are measured. In the calculation
 204 performed here to estimate total adsorbed amounts from excess adsorbed amounts, we
 205 adopt the procedure proposed by *Ottiger et al.* [2006]. We thus neglect the effect of
 206 mesopores and adsorption-induced deformations on the adsorption process, which is a
 207 very simplistic approach. However, correctly interpreting gravimetric adsorption data
 208 by taking into account the full coupling between adsorption and strain still remains a
 209 challenging issue. While this issue is not fully solved, in addition to the interpretation
 210 proposed here, as alternatives, one can aim at using models based directly on excess
 211 adsorption data (e.g., *Vermorel et al.* [2013a, b]) or instead at measuring total adsorbed
 212 amounts directly (e.g., as proposed by *Hol et al.* [2011]).

213 In order to bound the inverted parameters, we follow two paths for the inversion pro-
 214 cedure. First, we explore the anisotropy of adsorption-induced strains, and conclude
 215 that assuming isotropic and pressure-independent adsorption stresses is reasonable for
 216 the analyzed coal and permits recovering a plausible estimate of the coal mechanical
 217 anisotropy. Second, mechanical isotropy is assumed and the adsorption-strain coupling
 218 coefficients are recovered (still considered pressure-independent), so that, the anisotropy

of adsorption-strain coupling coefficients is determined. Last, we show that introducing a pressure-dependent coupling coefficients $c_1(p) \neq c_3(p)$ (based on the experimentally measured swelling strains and anisotropic mechanical elastic constants) enables a better the fitting of the experimental data.

3.1. Mechanical anisotropy and isotropic adsorption stresses

We first investigate whether adsorption-induced stresses can be assumed isotropic or not. According to our poromechanical model (Eq. 15), having equal coupling coefficients $c_1(p) = c_3(p)$ or equivalently $s_1^a(p) = s_3^a(p) = s^a(p)$ leads to,

$$\begin{cases} \varepsilon_1 = [s^a(p) - p] \left(\frac{1-\nu}{E} - \frac{\nu_3}{E_3} \right) \\ \varepsilon_3 = [s^a(p) - p] \left(\frac{1-2\nu_3}{E_3} \right) \end{cases} \quad (16)$$

which means that under such an assumption the ratio $\varepsilon_1/\varepsilon_3 = f(E, E_3, \nu, \nu_3)$ should be constant and independent of gas pressure and adsorption stresses. Figures 1-b and 1-e show the experimental ratios between the principal strains for both specimens. It is observed that $\varepsilon_1/\varepsilon_3$ and $\varepsilon_2/\varepsilon_3$ decrease slightly with pressure by about $\sim 10\%$ for fluid pressure $p < 10$ MPa, which indicates slight anisotropy of adsorption stresses only in this range of pressure. Hence, as a first approximation we set adsorption stresses equal in all directions $s_1^a = s_3^a = s^a$ with constant adsorption coupling functions so that $c_1(p) = c_3(p) = c$. Assuming isotropic adsorption stresses leads to recovering an upper bound for mechanical anisotropy, which can be assessed by the parameter $(C_{11} - C_{33})/(2C_{33})$. Additional assumptions help reduce the number of inverted parameters: non-diagonal stiffness coefficients are approximately equal $C_{12} \sim C_{13}$ (as observed in many shales with weak anisotropy from an extensive data compilation by Wang [2002]), and one of the

238 Poisson ratios is assumed $\nu_3 = 0.28$ according to typical coal Poisson ratios determined
 239 indirectly from elastic waves velocity [Morcote *et al.*, 2010].

240 By assuming $C_{12} \sim C_{13}$, the following moduli ratio holds,

$$\frac{E}{E_3} = \frac{\nu_3 + \nu_3\nu - \nu}{\nu_3^2} \quad (17)$$

241 hence, given ν_3 , $\nu = f(E/E_3)$. Given the total adsorbed amount and swelling principal
 242 strains of coal immersed in CO₂ as a function of pressure (ε_1 , ε_2 , ε_3), and a coupling
 243 coefficient c , the parameters n_0^{max} and β can be determined to best fit Eq. (9). Therefore,
 244 the free fitting parameters are E , E_3 , and c . The shear modulus in planes which contain
 245 the symmetry axis G_3 is not needed for this particular application.

246 We fit our model simultaneously to the swelling strain and total adsorption amount data
 247 by forward simulation and 2-norm error estimation. Modeled strains ε_1 and ε_3 are set to
 248 fit experimentally measured $(\varepsilon_1 + \varepsilon_2)/2$ and ε_3 respectively. The calculated error surfaces
 249 are available as Auxiliary Material. Figures 1-a,c,d,f show the best-fitting modeling results
 250 along with the experimental data and best fitting parameters. Notice that E and E_3 are
 251 the specimen “dry” or “drained” moduli. The unjacketed response of the same specimens
 252 to Helium (specimen 364-1: $d\varepsilon_3/dp = 0.0050$ %/MPa, $d\varepsilon_1/dp \sim 0.0040$ %/MPa; specimen
 253 364-2: $d\varepsilon_3/dp = 0.0049$ %/MPa, $d\varepsilon_1/dp \sim 0.0040$ %/MPa - original data set from *Hol and*
 254 *Spiers* [2012]) suggests stiffer moduli in the direction parallel to the bedding plane. From
 255 our inversion results, we indeed find that $E > E_3$. The inverted mechanical anisotropy in
 256 terms of the Thomsen parameter $\varepsilon^* = (C_{11} - C_{33})/(2C_{33})$ is about 0.137 (specimen 364-1)
 257 and 0.082 (specimen 364-2), in agreement with Thomsen parameters measured in other
 258 coals $\varepsilon^* \sim 0.05 - 0.10$ [Morcote *et al.*, 2010] and shales $\varepsilon^* = 0.17 \pm 0.08$ [Wang, 2002].

259 Inverted bulk moduli $K=4.21$ GPa for specimen 364-1 and $K=3.58$ GPa for specimen 364-
 260 2 are in the range of values for bituminous coal: 0.79 to 5.3 GPa (spanning several scales
 261 and loading rates [*Mazumder, 2007; Morcote et al., 2010; Pan et al., 2010; Masoudian*
 262 *et al., 2013*]).

3.2. Mechanical isotropy and anisotropic adsorption stresses

263 Let us now assume isotropic mechanical properties and find the pressure-independent
 264 adsorption-strain coupling coefficients c_1 and c_3 which best fit the experimental data.
 265 Having $E = E_3$ and $\nu = \nu_3$, Eq. (15) leads to

$$\begin{cases} \varepsilon_1 = \frac{1-\nu}{E} [s_1^a(p) - p] - \frac{\nu}{E} [s_3^a(p) - p] \\ \varepsilon_3 = -\frac{2\nu}{E} [s_1^a(p) - p] + \frac{1}{E} [s_3^a(p) - p] \end{cases} \quad (18)$$

266 We simplify the problem similarly as done above by assuming one known Poisson ratio
 267 $\nu = 0.28$. Forward simulation and error estimation let us recover the best fitting parameters
 268 E , c_1 , and c_3 . Figure 2 shows the simulation results for the best fitting parameters.
 269 Auxiliary Material contains the error surfaces for best fitting parameter determination.
 270 The fact that $c_3 > c_1$ implies that adsorption stresses would be higher in the direction
 271 perpendicular to the bedding plane. We find that the upper bound for adsorption stress
 272 anisotropy is $(c_3 - c_1)/(2c_1) \sim 0.048$ for specimen 364-1 and 0.030 for specimen 364-2. The
 273 fitting is overall poorer than the one observed by concentrating anisotropy on mechanical
 274 elastic moduli.

3.3. Pressure-dependent adsorption-strain coupling coefficients

275 Let us use now the values of E_3 , E , ν_3 , and ν found in Section 3.1 and relax the previous
 276 assumption of pressure-independent coupling coefficients. By taking the derivatives of Eq.

277 (15) with respect to pressure and multiplying by the inverse of the compliance matrix,
 278 the following holds,

$$\begin{bmatrix} \frac{ds_1^a(p)}{dp} - 1 \\ \frac{ds_3^a(p)}{dp} - 1 \end{bmatrix} = \begin{bmatrix} \frac{1-\nu}{E} & -\frac{\nu_3}{E_3} \\ -2\frac{\nu_3}{E_3} & \frac{1}{E_3} \end{bmatrix}^{-1} \begin{bmatrix} \frac{d\varepsilon_1}{dp} \\ \frac{d\varepsilon_3}{dp} \end{bmatrix} \quad (19)$$

279 Hence, calculating the value of $ds_i^a(p)/dp$, the coupling coefficients follow from Eq.
 280 (12) and are equal to $c_i(p) \sim 8$ to 11 (Figure 3-a,c - Note: $d\varepsilon_1/dp$ is calculated from
 281 experimental $(\varepsilon_1 + \varepsilon_2)/2$ as a function of pressure). The difference between $c_3(p)$ and
 282 $c_1(p)$ is maximum at pressure $p < 10$ MPa as suggested by Figure 1. The lower bound for
 283 anisotropy of adsorption stresses is estimated with the average difference $\overline{|c_3 - c_1|}/(2\overline{c_1})$
 284 equal to 0.013 for specimen 364-1 and 0.011 for specimen 364-2. We find that assuming
 285 a constant coupling coefficient with pressure does not capture perfectly the coal matrix
 286 linear compressibility observed experimentally at high pressures $p > 10$ MPa (See Figures
 287 1-a-d). In contrast, a better curve matching is observed by considering pressure-dependent
 288 coupling coefficients $c_1(p) \neq c_3(p)$. The recalculated swelling strains are plotted with the
 289 refitted adsorption variables n_0^{max} and β in Figure 3-b,d for both specimens.

4. Discussion

4.1. Comparison with empirical approaches and non-empirical theories

290 Early empirical developments simplify the effect of coal swelling in reservoir geome-
 291 chanics to be analogous to that of thermal dilation [*Palmer and Mansoori, 1998; Shi and*
 292 *Durucan, 2004*], such that, coal swelling is expressed empirically by fitting a Langmuir
 293 isotherm directly to swelling strains, or assuming a linear relationship between swelling
 294 and Langmuir-fitted adsorption amount (See a comprehensive review in *Pan and Connell*

295 [2012]). Such empirical developments are sometimes too simplistic, as here for instance,
 296 monotonic Langmuir functions would not be able to fit well the non-monotonic swelling
 297 strains shown in Figure 1.

298 Other non-empirical models have been recently proposed to explain and predict the
 299 adsorption-induced swelling of coal. First, *Hol and Spiers* [2012] proposed a thermody-
 300 namical model to explain the Brzeszcze coal swelling data we use in this article. They base
 301 their formulation on the separation of adsorption-induced swelling and bulk fluid-driven
 302 compression (similar to Eq. 15), with the additional hypothesis of a linear relationship
 303 between total adsorption amount and adsorption strain. Our model shows fair agreement
 304 with this hypothesis for samples immersed in the adsorbate at low gas pressure $p < 10$
 305 MPa, although deviations may occur at higher pressures when the bulk fluid pressure
 306 compression of the coal matrix prevails decreasing the total amount of adsorption (Figure
 307 1-c,f). Anisotropy modeling is not included by *Hol and Spiers* [2012], although it has
 308 been considered by the same authors elsewhere [*Hol et al.*, 2012]. Second, *Vermorel et al.*
 309 [2013a] developed a poromechanical formulation based on properties defined at the molec-
 310 ular scale, such as microporosity or microporous skeleton stiffness K_s . This formulation
 311 proposes an adsorption-mechanical coupling based on the definition of an apparent micro-
 312 porosity which depends on excess n_{ex} and total n_t adsorbed amounts. We find the isotropic
 313 version of our formulation compatible with theirs if $\partial n / \partial \epsilon|_p = (1 - K/K_s)n_t / (n_t - n_{ex})$
 314 where ϵ is the volumetric deformation (see Eq. 11). Third, *Pan and Connell* [2011] de-
 315 veloped a swelling model for mesoporous solids which includes orthotropy. They base
 316 their model on a crossed-tube analogous structure. In contrast, our model does not as-
 317 sume a particular geometry and mechanical properties ensues naturally from continuum

318 mechanics. Last, *Coudert et al.* [2011] present a general thermodynamical formulation
 319 of adsorption-strain couplings in soft microporous zeolites and metal organic frameworks.
 320 Their formulation shares many common points with our model.

321 All these non-empirical models have shown an advance in adsorption-strain understand-
 322 ing and good fitting results. We believe our model is thermodynamically and mechan-
 323 ically rigorous, based on well-defined quantities, valid for any strain or stress boundary
 324 conditions, and easily expandable to more complex constitutive laws (orthotropy, non-
 325 linearity). Our theoretical model has the key advantage over empirical developments of
 326 having fully coupled equations which relate adsorption not only to strain but also to stress.
 327 Furthermore, our model enables the prediction of the influence of adsorption on strains
 328 and stresses as well as the influence of stresses and strains on the amount of adsorbed
 329 fluid. The prediction of stresses is advantageous to use permeability-stress laws instead
 330 of permeability-porosity laws.

4.2. Adsorption isotherms for samples immersed in the adsorbate

331 We emphasize that adsorption isotherms of free-swelling coal samples immersed in the
 332 adsorbate represent just one path on the multivariate adsorption isotherm $n(p, \varepsilon_{ij})$ which
 333 describes how total adsorbed amount depends on fluid pressure and solid strains. Thus,
 334 the measurements from this kind of experiments are only relevant to this pressure-strain
 335 path and are not representative of the adsorption isotherm with the real boundary in-situ
 336 conditions. As shown in Figures 1-c,f and 2-b,d, the difference in adsorbed amount for a
 337 coal sample immersed in CO_2 (displacement-unconstrained, free swelling) and coal sam-
 338 ple kept at zero strain is $\sim 20\%$. External confining stresses, estimated at about about
 339 ~ 90 MPa with our model, must be applied in order to prevent any deformation of the

340 Brzeszcze coal sample (CO₂ pressure $p = 10$ MPa - from $\varepsilon_{ij} = 0$ in Eq. 13). In-situ
 341 conditions lie in between these two scenarios. In general, the adsorption isotherm is a
 342 multivariate function which depends on pressure and strains. Hence, there may be ad-
 343 sorption/desorption at constant fluid pressure driven by strain changes such as mechanical
 344 stretching and compression (Eq. 11 - See experimental evidence in [*Hol et al.*, 2012; *Hol*
 345 *and Spiers*, 2012]).

4.3. Relation between volumetric strain and total adsorption for samples immersed in the adsorbate

346 Our model predicts an approximately linear relationship between total adsorption
 347 amount and strain when adsorption-induced swelling prevails for adsorption experiments
 348 with coal samples immersed in the adsorbate, i.e., at low-medium fluid pressure (Figure
 349 4-a,b, $p < 10$ MPa). However, as predicted by our model (no adsorption amount experi-
 350 mental data in this pressure range), total adsorption amount may decrease as bulk fluid
 351 pressure takes more relevance and compresses the coal matrix. Improved certainty in the
 352 determination of total adsorption amount n would help corroborate this last statement.
 353 Recall the fact that we follow a Lagrangian mechanical description, therefore, adsorption
 354 per unit volume of undeformed coal matrix [mol/L] may be converted to adsorption per
 355 unit mass [mol/kg] through the initial mass density [kg/L]. Recently published experi-
 356 mental data of simultaneous measurement of adsorption and swelling up to 15 MPa show
 357 a similar shape of the swelling-adsorption signature as the one predicted by our model
 358 before the onset of coal matrix contraction (see Fig. 8 from *Day et al.* [2008]). Other
 359 phenomena that may affect the shape of the adsorption-strain curve include creep at con-

stant Terzaghi's effective stress and coal matrix adsorption-induced softening [Czaplinski
and Holda, 1982; Hagin and Zoback, 2010; Masoudian et al., 2013].

4.4. Adsorption-strain coupling expressed with Biot-like coefficients

The Biot coefficient α was first defined as the ratio of change in fluid content ζ to
dilation ϵ in a jacketed (drained) test, such that for a conventional poroelastic material
 $\zeta = \alpha\epsilon$ [Biot and Willis, 1957]. Biot noted that α can also be identified to $1 - K/K_{sk}$
(where K and K_{sk} are the bulk moduli measured in drained and unjacketed conditions)
which provides a further interpretation of α different from the first definition. The fact
that they yield equal values results from the symmetry of the coefficients in the poroelastic
matrix and in turn from the existence of a thermodynamic potential with pressure p and
change in fluid content ζ as conjugate variables. In conventional poroelasticity the density
of the fluid into the porosity of the material corresponds to its bulk density, therefore, the
Biot coefficient α is less than 1 as the volume of fluid ζ entering the specimen during a
drained test cannot be greater than its dilation ϵ .

However, this is not the case in adsorptive materials such as coal where the density
of the adsorbed fluid can be much greater than the density of the bulk fluid. In the
framework of the theory developed here for transverse isotropic microporous solids, the
incremental amount of fluid content $d\zeta = d(n\bar{V}_b)$ during a jacketed test is (from Eq. 9)

$$d[n(p, \varepsilon_{ij})\bar{V}_b(p)] = b_1(p)d\varepsilon_1 + b_2(p)d\varepsilon_2 + b_3(p)d\varepsilon_3 \quad (20)$$

where $b_i(p) = c_i(p)n_0(p)\bar{V}_b(p)$ can be coined as a (tangent) Biot-like coefficient, consis-
tently with the first definition given by Biot. The fluid content $n\bar{V}_b$ is the volume (per

unit volume of coal) that the amount of adsorbed fluid would occupy in it were in bulk
 conditions. Therefore the volume change $d(n\bar{V}_b)$ can be much larger than the volumetric
 dilation increment $d\epsilon$ leading to coefficients $b_i(p)$ exceeding 1. This does not contradict
 thermodynamics. Due to the symmetry already discussed, this coefficient $b_i(p)$ can still be
 identified to $1 - K/K_{unj}$ which is equal to ds_i^a/dp here (Eq. 12), but the unjacketed bulk
 modulus $K_{unj}(p)$ does not reveal the solid stiffness alone. It is a macroscopic property
 which also accounts for the adsorptive properties of the fluid molecules onto the solid pore
 walls. *Vermorel et al.* [2013b] defines an analogous Biot-like pressure-dependent coefficient
 as $b(p) = b^\infty n_T(p)/[n_T(p) - n_{excess}(p)]$ where $b^\infty < 1$ is the asymptotic Biot coefficient
 obtained at high fluid pressure.

Given the coal adsorption properties (n_0^{max}, β, c_i) and the CO₂ bulk molar volume \bar{V}_b ,
 the Biot-like coefficient ranges from $b^t \sim 40$ to 1 for low CO₂ pressure $p = 0$ to ~ 10 MPa
 (adsorption prevails) and decreases asymptotically to ~ 0.74 as CO₂ pressure increases
 (plotted in Figure 4-c,d as solid line for pressure-independent c and as symbols for pressure-
 dependent $c_i(p)$). The $b(p)$ curve exhibits an inflexion point which roughly coincides with
 the limit between adsorption-dominated swelling $b > 1$ and bulk fluid-driven compression
 $b < 1$ (Figure 4-c,d).

Although they remain nontrivial, variations of the introduced Biot-like coefficients b_i
 with the fluid pressure are simpler than variations of the coupling coefficients c_i , in the
 sense that at least the former are monotonic. The complexity of the variations of the
 coefficients $c_i(p)$ stems from the fact that those coefficients involve characteristics of the
 solid, of the fluid, and of their interaction. In contrast, since $b_i(p) = c_i(p)n_0(p)\bar{V}_b(p)$, the
 Biot-like coefficients are corrected for variations of density of the bulk fluid. Therefore,

402 when looking for a physical interpretation of the inverted parameters of the model, one
 403 might find more useful focusing on the Biot-like coefficients rather than on the more
 404 convoluted coupling coefficients c_i . For instance, in the isotropic case, *Vermorel et al.*
 405 [2013b] propose the physical rule of thumb that the Biot-like coefficient $b(p)$ is proportional
 406 to the ratio of the density ρ_{sorbed} of the adsorbed phase to the density ρ_{free} of the bulk
 407 phase (i.e., $b(p) \propto \rho_{sorbed}(p)/\rho_{free}(p)$).

4.5. Implications for coal bed methane recovery

408 The determination of strains and effective stress on the direction of the bedding plane
 409 in coal seams subjected to primary or secondary methane recovery is critical to predict
 410 changes in fracture permeability. Various permeability-stress relationships have been pro-
 411 posed to predict permeability, generally in the form: $\log(k/k_0) = a(\sigma_h + p - \sigma_{h0} - p_0)$
 412 (being k_0 the reference permeability at total horizontal stress σ_{h0} and fluid pressure p_0
 413 and $a \sim 0.1$ to 0.2 MPa^{-1} [*Somerton et al.*, 1975; *Pan and Connell*, 2012]). Thus, a
 414 general model that predicts stresses in the anisotropic coal seam as a function of fluid
 415 pressure and boundary conditions is required for realistic predictions and simulations of
 416 coal bed methane recovery. The coal seam can be modeled as a double-porosity reservoir
 417 rock, where cleats account for macroporosity and coal matrix micropores account for the
 418 microporosity. In order to become practical at the scale of the seam, the constitutive
 419 laws derived here at the scale of the coal matrix must be upscaled to the scale of the
 420 coal seam by incorporating the presence of the cleats, in the spirit of what was done by
 421 *Nikoosokhan et al.* [2012]. In this upscaling, the presence of the cleats only induces regular
 422 poromechanical effects, in the sense that cleats are macropores in which adsorption-effects
 423 are negligible, and the coal matrix is responsible for adsorption-induced phenomena. This

424 extension of our model will allow to incorporate, in a thermodynamically sound manner,
425 both anisotropy and adsorption-induced phenomena into the constitutive laws of coal
426 seams.

5. Conclusions

427 Coal matrix is a natural disordered microporous solid. Material properties are often
428 anisotropic due to sedimentation and diagenetic processes. Although coal adsorptive
429 properties have been widely studied, the physical link between adsorption and induced-
430 strain has been relegated to a second plane. The knowledge of adsorptive and mechanical
431 properties is critical for calculating coal bed gas reserves and storage capacity, and enabling
432 predictable exploitability.

433 We extended a poromechanical model developed for microporous solids to take into
434 account adsorptive-mechanical anisotropy through adsorption stresses and a stiffness ma-
435 trix. Our model ensues from first principles and continuum mechanics, and applies to any
436 displacement or stress boundary conditions.

437 Experimental data from the literature help validate our model and invert adsorptive-
438 mechanical model parameters. The model is able to simulate the competition between
439 adsorption-induced adsorption and bulk fluid-driven compression in adsorption experi-
440 ments of coal samples immersed in CO₂.

441 Remarkable lessons from this study and the Brzeszcze coal include: (1) swelling
442 anisotropy is likely to be caused principally by mechanical anisotropy ($E > E_3$), in
443 fact, concentrating anisotropy on elastic moduli yields better fitting than concentrat-
444 ing anisotropy on adsorption stresses, (2) assuming a coupling coefficient c independent of
445 fluid pressure is reasonable and yields acceptable predictions, (3) adsorption measurements

446 in coal samples immersed in the adsorbate represent just one path on the multivariate
447 adsorption isotherm.

448 The developed fully coupled model permits inverting transverse isotropic mechanical-
449 adsorptive properties of microporous coal matrix. Upscaling to a coal seam model which
450 includes both macroporous cleats and microporous adsorptive coal matrix would yield the
451 coupled constitutive equations of the coal seam. This set of fully coupled equations enable
452 the prediction of strains and effective stress in different directions respect to the bedding
453 plane under in-situ anisotropic state of stresses. The calculated effective stresses can be
454 used through permeability-stress relationships for determining seam permeability.

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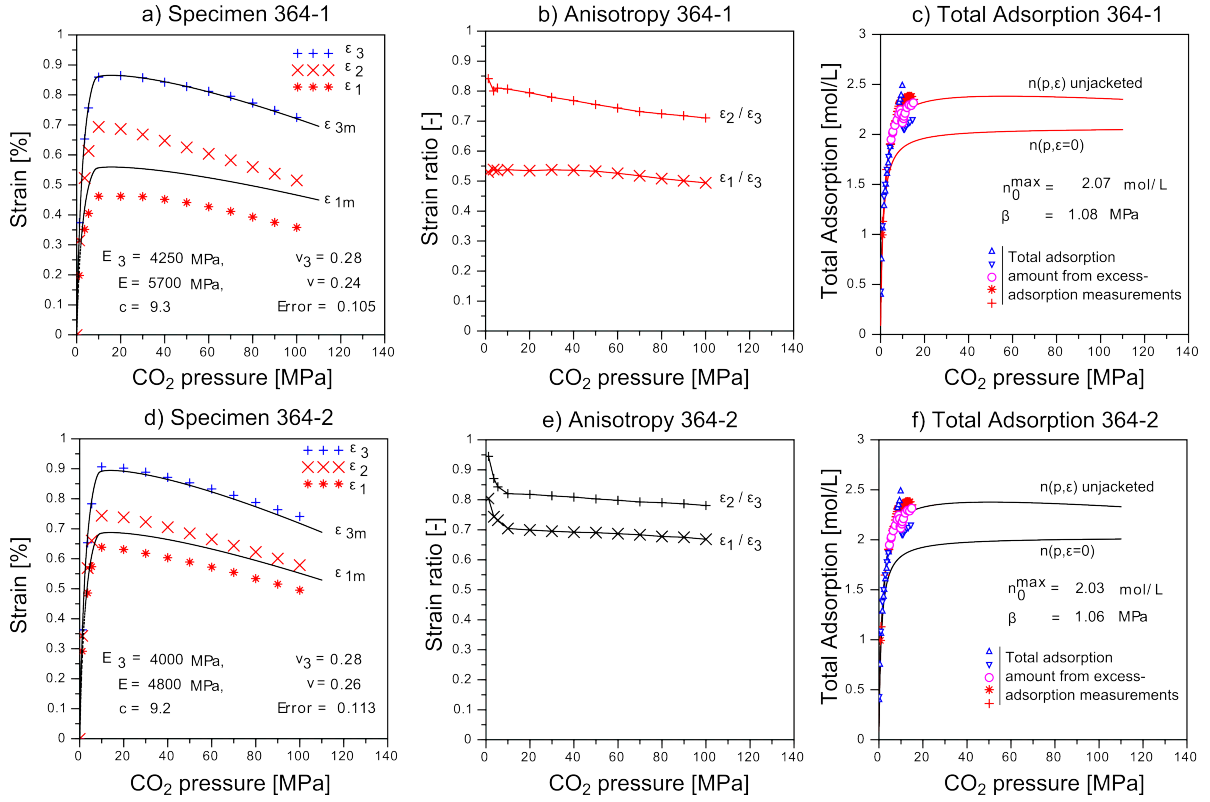


Figure 1. Adsorption-induced swelling of coal immersed in CO₂. (a) Experimental measurements (symbols: principal strains $\epsilon_1, \epsilon_2, \epsilon_3$ - original data set from *Hol and Spiers* [2012]) and transverse isotropic microporous model predictions considering mechanical anisotropy only $c_1(p) = c_3(p) = c$ (lines: $\epsilon_{1m}, \epsilon_{3m}$ fit $(\epsilon_1 + \epsilon_2)/2$ and ϵ_3 respectively). (b) Swelling anisotropy: strain ratios ϵ_1 and ϵ_2 respect to the major principal strain ϵ_3 perpendicular to the bedding plane. (c) Total adsorption amount estimated from excess sorption measurements (symbols - see Auxiliary Material) and model fitted prediction (Eq. 9). (a,b,c) Specimen 364-1. (d,e,f) Specimen 364-2.

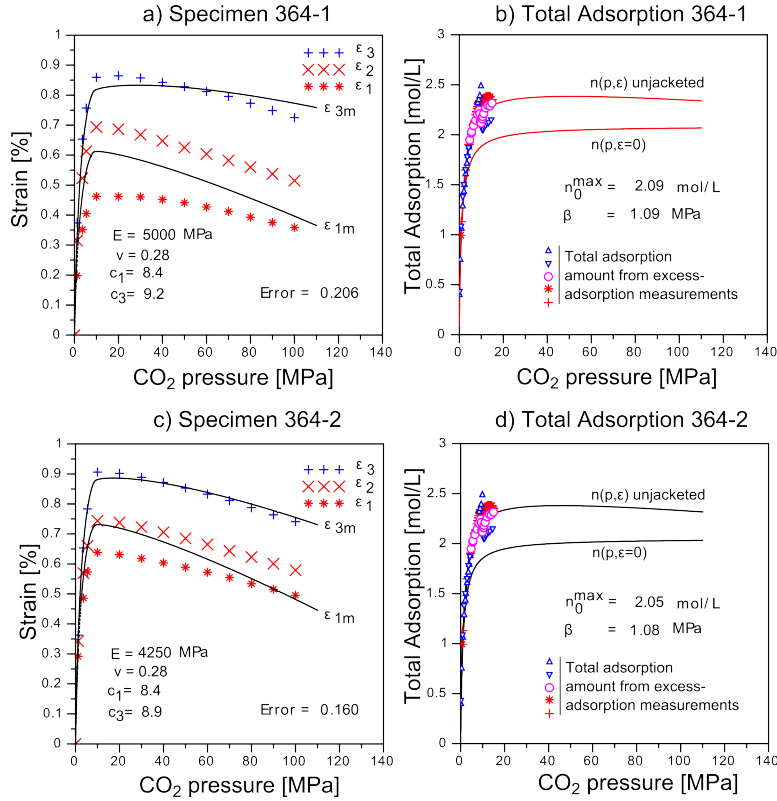


Figure 2. Adsorption-induced swelling of coal immersed in CO₂. (a) Experimental measurements (symbols: principal strains $\epsilon_1, \epsilon_2, \epsilon_3$ - original data set from *Hol and Spiers* [2012]) and transverse isotropic microporous model predictions considering anisotropy on adsorption stresses only $E = E_3$ and $\nu = \nu_3$ (lines: $\epsilon_{1m}, \epsilon_{3m}$ fit $(\epsilon_1 + \epsilon_2)/2$ and ϵ_3 respectively). (b) Total adsorption amount estimated from excess sorption measurements (symbols - Auxiliary Material) and model fitted prediction (Eq. 9). (a,b) Specimen 364-1. (c,d) Specimen 364-2.

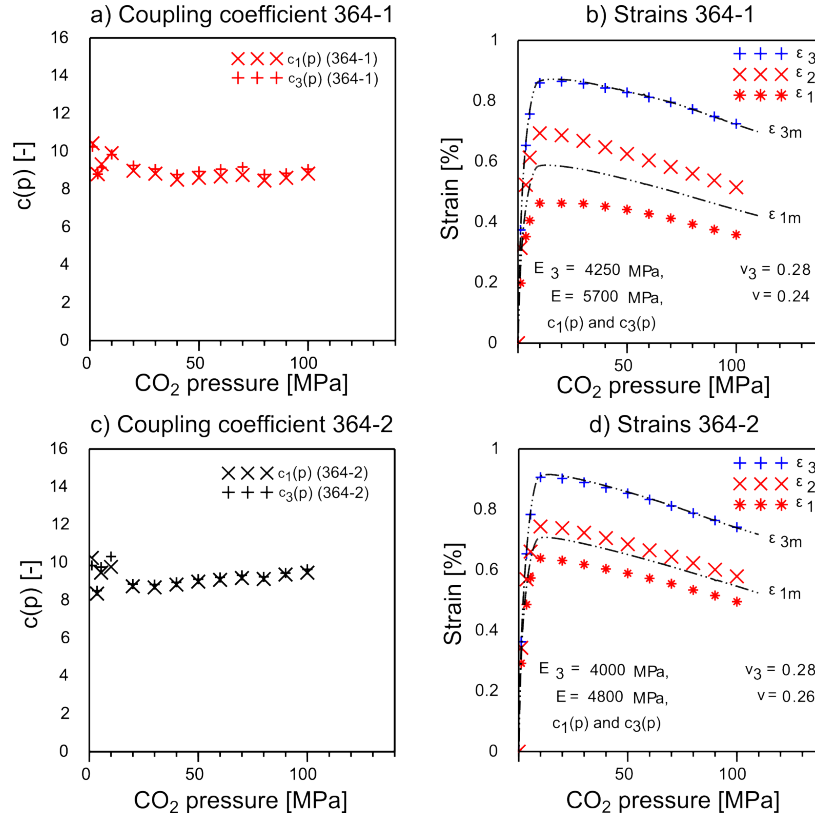


Figure 3. Determination of adsorption-strain coupling coefficients as a function of pressure for finding minimum adsorption stress anisotropy. (a) Calculated coupling coefficient $c_i(p)$ in the bedding plane and perpendicular to the bedding plane (Eq. 19). (b) Transverse isotropic microporous model predictions (lines: $\epsilon_{1m}, \epsilon_{3m}$) considering $c_i(p)$ previously calculated and refitted n_0^{max} and β compared to experimental data - original data set from *Hol and Spiers* [2012]. (a,b) Specimen 364-1 - refitted $n_0^{max} = 2.04$ mol/L and $\beta = 1.08$. (d,e) Specimen 364-2 - refitted $n_0^{max} = 2.00$ mol/L and $\beta = 1.06$.

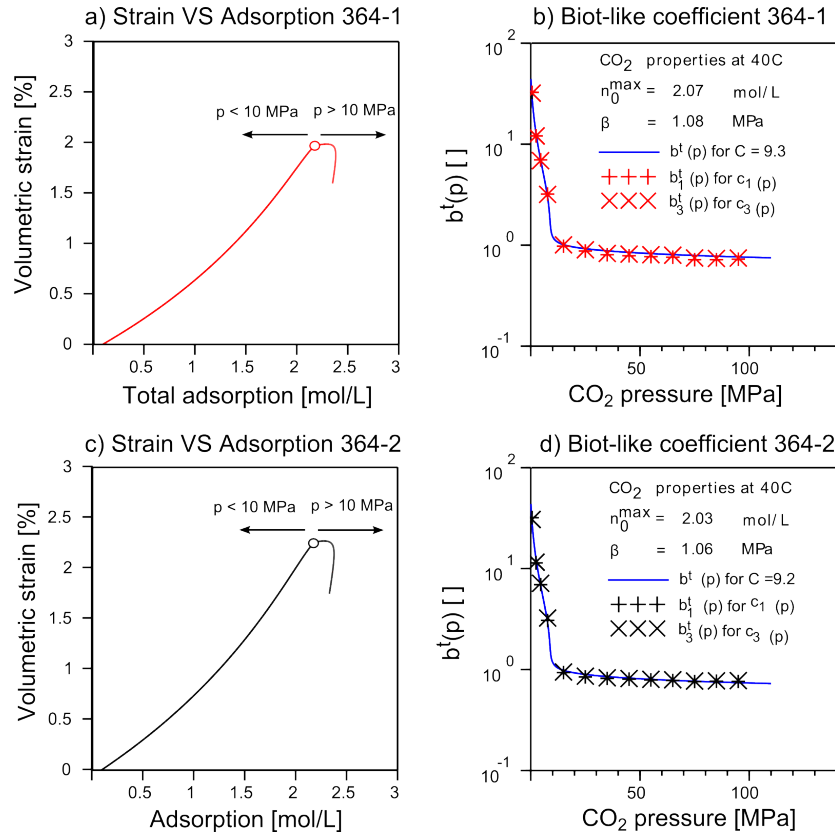


Figure 4. Insight into the poromechanics of coal matrix. (a) Model-predicted volumetric strain as a function of total adsorption amount for coal immersed in CO_2 (model parameters from Figure 1). (b) Biot-like pressure dependent functions $b_i^t(p)$. (a,b) Specimen 364-1. (c,d) Specimen 364-2.