Adsorption-Induced Swelling of Porous Media

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ABSTRACT

This paper studies deformation and swelling of porous media induced by sorption of fluids, and in particular carbon dioxide. The phenomena are significant, not only to the capacity of porous formations for storing CO₂, but also to the effect that they have on the mechanical properties of the formations and microseismic events that they might possibly trigger. To study the phenomena we formulate the problem by energy consideration in which the Hamiltonian (total energy) of a porous medium and its fluid content is represented as the sum of the elastic energy of the system, and the energies associated with the interactions between the adsorbates and between them and the medium's solid matrix. The gas phase is described by a density functional theory, while the solid matrix can be either linearly or nonlinearly elastic. The model provides predictions for the sorption isotherms, the dependence of the strain on the bulk pressure, and the change in the porosity. The change in the strain is anisotropic due to the deformation of the solid, as well as the difference between the stiffness of the matrix and the fluid phase. During desorption the strain is also released and, similar to the sorption isotherms, exhibits hysteresis. This opens up the possibility of using mechanical measurements during sorption experiments to gain insight into the structure of a porous medium. When the model was applied to sorption of CO₂ in clay particles, all the reported experimental features of the phenomena were reproduced.

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1. Introduction

Swelling of porous materials due to their liquid content, or by storage of gases in their pore space, is a widespread phenomenon. Print papers swell when they come into contact with water, or even by the coating fluid that makes high quality surface (Ghassemzadeh *et al.*, 2001). In biomedical science the interactions between ions and charged proteoglycans govern the deformation of cartilaginous soft-hydrated tissues. Swelling of polymers and biopolymers have numerous applications, ranging from size-exclusion chromatography, to efficient materials for drug delivery, gel electrophoresis during filtration processes, contact lenses, and food stuff.

An important class of porous media to which swelling is important is that of natural geo-materials. For example, porous formations that contain charged molecules and brine may swell if penetrated by fresh water. Moreover, swelling of smectite clays by water has been studied for decades. Clay swelling is of critical importance to geotechnical and geoenvironmental fields, as it may cause damage to the foundations of buildings, giving rise to cracks and displacements of footings. These are irreversible phenomena with considerable economic implications. Bentonitic-based compacted clays have low hydraulic conductivity, plasticity (Benson *et al.*, 1994), swelling and adsorptive capacity for contaminants, which is why they are used as sealing materials to prevent leaking of contaminants to the environment. Storage of radioactive nuclear wastes in geological formations is perhaps the only viable solution to problem of safeguarding such materials, and compacted clays may be used for sealing the storage area. Yet another example is provided by gas-bearing shales that represent unconventional sources of energy that have attracted wide attention. Their swelling is a major negative factor during drilling, as it can cause significant problems for wellbore stability.

A more recent problem in which swelling of porous media is important is sequestration of carbon dioxide in geological formations, such as depleted oil and gas reservoirs, and unminable coal seams (Michels *et al.*, 2015; de Jong *et al.*, 2014; Hemmen *et al.*, 2012; Loring *et al.*, 2012; Tsotsis *et al.*, 2004; Yang *et al.*, 2011; Billefont *et al.*, 2013; McDonald *et al.*, 2015; Cho *et al.*, 2015; Dadwhal *et al.*, 2008), as well as in metal-organic frameworks and other types of adsorbents that have been fabricated for capturing CO₂ (Sumida *et al.*, 2012). The main characteristics of the geological formations for long-term CO₂ geo-sequestration include high storage capacity and effective sealing of the caprocks that are composed frequently of shale

and, thus, clay minerals. The low permeability of the clay formations reduces the possibility of upward migration of CO_2 in the formations and its penetration into the neighboring natural resources (Shukla *et al.*, 2010).

Clay minerals are typically composed of smectite, kaolinite, chlorite and illite (Loring *et al.*, 2014; Gasparik *et al.*, 2014), among which smectite has the highest sorption capacity due to their high internal surface area (Ji *et al.*, 2012). Busch *et al.* (2008) studied CO_2 sorption in a shale sample and various clay minerals in order to investigate the storage capacity and sealing integrity of such formations. They reported that clay minerals, especially montmorillonite, have significant sorption and storage capacity for CO_2 .

More generally, numerous experimental studies have been carried out to understand adsorption of CO_2 in porous media. For example, a study by Ravikovitch *et al.* (2005) on adsorption of CO_2 in soil samples containing various organic matters at 273 K and low pressures indicated that CO_2 tends to adsorb onto the domain of soil that is rich in organic matter. In another experimental study of CO_2 storage in organic-rich shale samples, it was found that even such formations that are nearly impermeable and have low porosity are capable of storing a remarkable amount of CO_2 , which was attributed to the finely-distributed organic nanopores (Kang *et al.*, 2011). Many careful and precise experiments, as well as theoretical studies have also been reported on the effect of CO_2 sorption in coal (Vandamme *et al.*, 2010; Hol *et al.*, 2011, 2012; Hol and Spiers, 2012).

Theoretical and computational studies of fluid sorption in porous media have also been carried out, including lattice density functional theory (DFT) (Pan and Connell, 2007; Ottiger *et al.*, 2008; Woo *et al.*, 2001), quenched solid DFT (Yang *et al.*, 2011; Gor and Neimark, 2011), nonlocal DFT (Ravikovitch and Neimark, 2006), thermodynamic models (Grosman and Ortega, 2008; Kulasinski *et al.*, 2015b; Liu *et al.*, 2015), and molecular dynamics (MD) (Ghassemzadeh *et al.*, 2000; Xu *et al.*, 2001; Ghassemzadeh and Sahimi, 2004; Kim *et al.*, 2005, 2007; Liu and Bhatia, 2013; Rao and Leng, 2016) and Monte Carlo simulations (Valiullin *et al.*, 2006).

Adsorption of gases in a porous matrix leads to its swelling, which affects the porosity, permeability, diffusivity, and surface area of the pore space (Perera *et al.*, 2011; Ozdemir and Schroeder, 2009), and has been studied both experimentally and theoretically (Ravikovitch and Neimark, 2006; Grosman and Ortega, 2008; Balzer *et al.*, 2011). For example, a combined experimental and modeling study of adsorption of CO_2 and N_2 in coal samples has been reported,

which demonstrated that volumetric strain caused by gas adsorption leads to reduction of the permeability (Pini *et al.*, 2009). Another experimental study of coal swelling in response to CO₂ adsorption by Anggara *et al.* (2014) demonstrated that coal tends to swell anisotropically. The maximum volumetric swelling ranged from 1.60 to 2.35 percent. Recent molecular MD simulation of diffusion and adsorption of CO₂ in Montmorillonite structures as the model of clay minerals indicate that the basal spacing of the material changes (Dashtian *et al.*, 2016). Pan and Connell (2007) developed a theoretical framework based on energy consideration to describe volumetric changes in coal due to gas adsorption. Their model was capable of predicting changes in the porosity and permeability of coalbeds as a result of swelling or shrinkage by gas adsorption. Vandamme *et al.* (2010) developed a model capable of calculating the macroscopic strains in response to adsorption in a porous medium. Using a thermodynamic framework, they developed the poromechanics of the process by considering the surface energy. The surface stress was modified by adsorption, a phenomenon that has also been studied by molecular dynamics simulation (see above). A thermodynamic framework was also developed by Hol *et al.* (2012) that modeled adsorption of CO₂ by unconfined and confined coal. They combined their model with poroelasticity and studied the competition between adsorption-induced strain and poroelastic strain in terms of the applied external stress, fluid pressure and concentration. In a study by Espinoza *et al.* (2013) a poromechanical model for adsorption and strain was developed. Their model predicted that strain anisotropy is essentially due to anisotropy in the mechanical properties of porous solid.

Several studies of swelling induced by CO₂ sorption have been reported in coal samples (Yang *et al.*, 2011; Kim *et al.*, 2011; Kowalczyk *et al.*, 2010), as well as in clay minerals and shales (Giesting *et al.*, 2012; Rother *et al.*, 2013; Kadoura *et al.*, 2016; Rao and Leng, 2016). One such study was reported by Heller and Zoback (2014) who carried out experiments on the adsorption capacity of CO₂ and CH₄ of shale samples from four reservoirs, as well as pure illite and kaolinite. Their study indicated that gas adsorption causes a volumetric swelling strain on the order of 10^{-5} to 10^{-3} . In a more recent study swelling of shales as a result of CO₂ adsorption was investigated. All the samples studied exhibited anisotropic strain caused by CO₂ adsorption (Lu *et al.*, 2016).

In terms of deforming rock - but not the mechanism by which the deformation is achieved - sorption-induced deformation of porous materials is somewhat similar to subsidence of oil

and gas reservoirs (Doornhof *et al.*, 2006). The mechanism of the two are, of course, different. Sorption-induced deformation is due to the chemical potential of the sorbing species, whereas subsidence is due gas pressure reduction. Flow of oil or gas in some reservoirs causes deformation, compaction and subsidence in the reservoir. Thus, to model such phenomena one must couple the elastic or elasto-plastic equations governing the deformation to the equations of hydrodynamics governing fluid flow. In a similar spirit, any reasonable model of sorption-induced swelling of a porous medium must couple the elastic deformation of the solid to the thermodynamic state of the fluid in the pore space, the chemical potential of the sorbing species, and the interactions between the solid and the gas (Chin and Nagel, 2004; Guyer and Kim, 2015; see also Vandamme *et al.*, 2010; Hol *et al.*, 2012; Espinoza *et al.*, 2013).

The goal of this paper is to present and use one such model by coupling the lattice gas DFT with the equation for elastic deformation and finite-element (FE) computations in order to study adsorption-induced swelling in a disordered porous medium, and in particular clay particles. We use the model to study sorption of CO₂ in clay minerals and its effect on their swelling.

The rest of this paper is organized as follows. In the next section we describe the details of the model for calculating the adsorption isotherms and the deformation strains. Next, the details of the numerical simulations are presented. The model is then applied to CO₂ sorption in clay and the resulting swelling and change in its porosity. The results are then presented and discussed. In particular, we study the effect of the model's parameters on sorption, strain and porosity. The extension of the model to changing the mechanical properties of porous media, as well as possible triggering microseismic events that have recently been reported, are discussed. We summarize the key conclusions in the last section.

2. The Model

Let us first state clearly our assumptions. We assume, (i) a quasi-static system, and (ii) a linearly-elastic solid matrix for the porous media (see also below). The coupling between the solid matrix and its deformation and the fluid, and the interactions between the two are formulated through the total energy E of the system (the porous media plus their fluid content). Thus,

$$E = E_f + E_s + E_{fs} , \tag{1}$$

where E_f , E_s , and E_{fs} denote, respectively, the energy due to the fluid, the solid, and the interactions between the two. Various expressions can be used for each of the three terms on the right side of Eq. (1). One of the simplest of such expressions for E_f is given by a mean-field DFT (Pitard *et al.*, 1995; Kierlik *et al.*, 1998; Kierlik *et al.*, 2001),

$$E_f = \frac{1}{\beta} \sum_i [\rho_i \ln \rho_i + (1 - \rho_i) \ln(1 - \rho_i)] - \frac{1}{2} \epsilon_{ff} \sum_i \sum_Z \rho_i \rho_{i+Z} - \mu \sum_i \rho_i, \quad (2)$$

where $\beta = (k_B T)^{-1}$, with k_B being the Boltzmann's constant, and T the temperature. The basis of Eq. (2) is a lattice-gas model in which each site i is occupied by only one species, and only nearest-neighbor interactions are allowed. Thus, Z is the coordination number of the structure or the lattice used (see below). In Eq. (2) μ is the external chemical potential, ρ_i is the average fluid density at site i , and ϵ_{ff} is the fluid-fluid interaction parameter. Each site i is characterized by two indicator functions I_i and $\mathcal{I}_i$, such that $I_i = 0$ and 1 and $(1 - \mathcal{I}_i) = 0$ and 1 represent respectively, the fluid and the matrix indicator functions, so that $\rho_i = \langle I_i \mathcal{I}_i \rangle$.

Since we assume that the solid matrix is linearly elastic, the expression for E_s is straightforward:

$$E_s = \frac{1}{2} \sum_i (K_i \varepsilon_i^2 + 2\sigma_i \varepsilon_i), \quad (3)$$

where K_i is the elastic stiffness, and ε_i and σ_i are the strain and stress at i , respectively. For linearly-elastic solids the relation between the strain and displacement is known and used here. But, the assumption of elastic linearity can also be relaxed, in which case Eq. (3) must be replaced with a constitutive equation for an elastically-nonlinear solid (Sahimi, 2003; Guyer and Johnson, 2009). It remains to specify the energy E_{fs} associated with the fluid-solid interactions. Clearly, E_{fs} consists of two terms:

$$E_{fs} = E_w + E_{ce}. \quad (4)$$

Here, E_w is associated with the “wetting energy” that is present at any fluid-solid interface, while E_{ce} is the change in the elastic energy as a result of the presence of the fluid. Thus, we write (Guyer and Kim, 2015),

$$E_w = -\frac{1}{2} \epsilon_{fs} \sum_i \rho_i, \quad (5)$$

$$E_{ce} = \frac{1}{2} \sum_i [\lambda_i \rho_i (\nabla \cdot \mathbf{u})_i], \quad (6)$$

where $\mathbf{u}$ is the displacement vector, ϵ_{fs} is a fluid-solid interaction parameter related to the wetting properties of the surface, while λ_i is a parameter associated with the change in the strain energy and deformation of the solid as a result of the fluid's presence. The sum is over all pairs of the lattice sites. The porous medium and its content are in fluid exchange with a reservoir at temperature T and chemical potential μ .

The physical meanings of the interaction parameters ϵ_{fs} and ϵ_{ff} are clear. They can be estimated by a mean-field theory (see below), or by direct MD computations. But, at first sight, it might not be clear how to estimate the parameter λ_i by MD simulations. Although in this paper we treat λ_i as an adjustable parameter, it can in fact be computed by MD calculations (efforts in this direction are underway), the procedure for which is as follows. Let L be the length of the pore or void in which the fluid resides. To estimate λ_i one needs some sort of representation of the pore, either as a collection of the atoms properly bound together to represent the solid, as in standard MD simulations, or a continuum representation of the pore. The mechanical state of the structure must be precisely and properly specified. Then, the fluid is introduced into the pore or void that is in equilibrium with the chemical potential reservoir (bulk state). The pore walls have an attractive potential that draws the fluid particles toward them. Thus, in principle, a well-defined thermodynamic state with energy $E(T, V, \mu)$ exists, where V is the volume. As the chemical potential μ is increased, the fluid's configurations change and try to contract/expand the pore length L . One monitors and computes the variations in L as a function of μ . Then, as Eq. (6) indicates, $\lambda_i = dL/d(mu)$, or equivalently, $\lambda_i = dL/dN$, where N is the number of particles on pore wall.

It would perhaps be useful to compare our approach with the previous works that also attempted to couple sorption with deformation. Prominent among such models is the work of Hol and co-workers. Hol *et al.* (2012) consider the Gibbs energy of the solid and the fluid phase and add them together to obtain an expression for the total energy of the system. By differentiating the total free energy of the system and considering the condition of equality of chemical potential of adsorbed CO_2 and the free CO_2 in the equilibrium state, they derived an equation that represents the equilibrium concentration of the adsorbed CO_2 . Then, by changing the fluid pressure at a constant temperature, the adsorbed concentration of CO_2 was computed at various pressures. Finally, the volumetric strain induced by the adsorption was calculated by using the adsorbed concentration of CO_2 and the molar volume of the adsorbed CO_2 .

To obtain the equilibrium state of the system, we minimize the total energy E with respect to the density and strain (displacement) to derive the governing equations for the local density and the displacement field. This is described next.

3. Numerical Simulation and Model Implementation

For a given realization of a porous medium and a specific *bulk* chemical potential μ that is in equilibrium with the pore space and its fluid content, the set of equations resulting from minimizing the total energy with respect to $\mathbf{u}$ and ρ_i must be solved numerically. The minimization yields the following equation for the fluid density ρ_i ,

$$\rho_i = \left\{ 1 + \exp \left(-\beta [\mu + \epsilon_{fs} + \epsilon_{ff} \sum_Z \rho_{i+Z} - \lambda_i (\nabla \cdot \mathbf{u})_i] \right) \right\}^{-1}. \quad (7)$$

For a given chemical potential μ we first provide guesses for ρ_i and $\mathbf{u}$ and substitute them in the right side of Eq. (7), which yields a new approximate solution for ρ_i , which enables us to discretize the second governing equation by the FE method using triangular elements and linear basis functions. The second equation (after minimizing the total energy) for the displacement $\mathbf{u}_l$ of vertex l in triangle i is given by,

$$\mathbf{k}_e \mathbf{u}_l = \frac{1}{2} \mathbf{e}_{ni} \lambda_i \rho_i, \quad (8)$$

where the $\mathbf{e}_{ni}$ are the three unit vectors from the center of triangular element i to its vertices n . Note that the right side of Eq. (8) is simply the force acting on the vertices of the triangular elements. The domain of the computations is a clay particle, including its pore and solid phases; see Fig. 1.

To proceed with computing the displacements, we first calculate the stiffness matrix of each FE triangular element. If a triangle's vertices are at (x_1, y_1) , (x_2, y_2) , and (x_3, y_3) , then its stiffness matrix $\mathbf{k}_e$ is given by

$$\mathbf{k}_e = \int_{\mathcal{S}} \mathbf{B}^T \mathbf{D} \mathbf{B} d\mathcal{S} = \mathcal{S} \mathbf{B}^T \mathbf{D} \mathbf{B}, \quad (9)$$

with $\mathcal{S} = \frac{1}{2}J = \frac{1}{2}(x_{13}y_{23} - x_{23}y_{13})$ being the triangular element's area, $\mathbf{D}$ the elasticity matrix, $\mathbf{B}$ the strain-displacement matrix, and T denoting the transpose operation. Here, $x_{ij} = x_i - x_j$

and similarly for y_{ij} . Then,

$$\mathbf{B} = \frac{1}{J} \begin{pmatrix} y_{23} & 0 & y_{31} & 0 & y_{12} & 0 \\ 0 & x_{32} & 0 & x_{13} & 0 & x_{21} \\ x_{32} & y_{23} & x_{13} & y_{31} & x_{21} & y_{12} \end{pmatrix}, \quad (10)$$

and

$$\mathbf{D} = \frac{Y}{(1+\nu)(1-2\nu)} \begin{pmatrix} 1-\nu & \nu & 0 \\ \nu & 1-\nu & 0 \\ 0 & 0 & \frac{1}{2}[1-2\nu] \end{pmatrix}, \quad (11)$$

where Y is the Young's modulus (bulk modulus for the fluid phase), and ν the Poisson's ratio. We then set up a global stiffness matrix $\mathbf{K}$ by compiling in it the stiffness matrices of the triangular elements, which gives rise to the following system of linear equations describing the displacements of elemental vertices:

$$\sum_l K_{nl} \mathbf{u}_l = \frac{1}{2} \sum_i \mathbf{e}_{ni} \lambda_i \rho_i. \quad (12)$$

The set (12) is solved by the conjugate-gradient method to obtain a new approximate solution for the displacements. We then substitute the new approximations in the right side of Eq. (7) to obtain the next approximate solution for ρ_i , return to Eq. (12) to compute the new displacements, and continue the iteration until ρ_i and the displacements no longer change between the iterations. Periodic boundary conditions were used for computing the density field. As for the displacement field, we used a free-displacement boundary condition. This was meant to mimic the conditions under which the experimental data with which we compare the model's predictions were measured. In the experiments (Michels *et al.*, 2015) the sample was in contact with a bath of CO_2 , unlike a reservoir condition under compaction with an external stress applied to the external surface of the particle. The corresponding porosity ϕ of the pore space and the pressure-dependence of the strain are then computed.

Note that each FE triangular element is either filled by the fluid or represents the solid matrix. To begin the iteration process for solving the set of equations (7) and (12), a uniform density profile was used as the initial approximation. In order to compute the adsorption isotherms, the chemical potential was increased incrementally from a very large negative value to the bulk chemical potential. In the present work we consider 2D disordered porous media, as the experimental data that we used to determine some of the parameters of the model were

for a thin, essentially 2D medium (see below). But, it would pose no particular difficulty to use a 3D model. The number of the triangles representing the solid matrix was selected so that the porosity of the model pore space matches that of the porous medium with which we compare the results.

3. Results

We have used the model to study a variety of cases. In what follows we present and discuss the results.

3.1 Estimating the model's parameters

The model is general in that, given expressions for the various types of energies described in the last section, it can be applied to adsorption-induced swelling in any porous material. Our main interest in this paper is, however, in the adsorption of CO_2 in clay particles. As usual, the sorption isotherms are obtained by computing the overall density of CO_2 in the pore space, $\rho_{\text{CO}_2} = N^{-1} \sum_i \rho_i$ as a function of the pressure P at a temperature below the bulk critical temperature, with N being the total number of sites in the pore space. In addition, we compute the variations of the strain and the porosity during sorption. The excess adsorption is calculated by,

$$\rho_{\text{ex}} = \frac{1}{N} \sum_i (\rho_i - \rho_b) , \quad (13)$$

where ρ_b is the density of the bulk fluid. The properties of the bulk fluid are given by (Monson, 2012),

$$\phi_p N = -N k_B T \ln(1 - \rho_b) - \frac{1}{2} Z N \epsilon_{ff} \rho_b^2 , \quad (14)$$

$$\mu_b = k_B T \ln \left(\frac{\rho_b}{1 - \rho_b} \right) - Z \epsilon_{ff} \rho_b , \quad (15)$$

where $\phi_p = P v_s$ is the lattice equivalent of the bulk pressure, and v_s is the physical volume equivalent to a lattice site. Equations (14) and (15) are for the lattice-gas model.

The interaction parameters ϵ_{ff} and ϵ_{fs} , the strain energy parameter λ_i , and the maximum pore-filling capacity that is required for converting the physical units of the experimental data for sorption to lattice gas units must be determined. According to the mean-field theory, the bulk critical temperature is given by

$$T_c = \frac{Z \epsilon_{ff}}{4 k_B} , \quad (16)$$

and, thus, the fluid-fluid interaction parameter is given by, $\epsilon_{ff}/k_B = 4T_c/Z$. With CO₂ being the adsorbate we obtain, $\epsilon_{ff}/k_B \approx 405.67$ K, if we use $T_c \approx 304.25$ and $Z = 3$ for CO₂. The maximum pore-filling capacity is $n_{\max}v_p$, where $n_{\max}$ is the maximum fluid density, and v_p is the pore volume. We first estimate the range of variations of $n_{\max}$. The minimum value of $n_{\max}$ is estimated by the inverse of the van der Waals co-volume, which for CO₂ is 1.03 gr/cm³. Its maximum is estimated as $\sqrt{2}/\sigma^3$, the density of a close packing of spheres, where σ is the molecular diameter. Therefore, the upper limit of $n_{\max}$ for CO₂ is (Woo *et al.*, 2001) 1.74 gr/cm³. Thus, $n_{\max}$ varies by a factor less than 2. In fact, the theoretical sorption isotherm is not sensitive to $n_{\max}$. Our preliminary simulations indicated that the lower limit of $n_{\max}$ provides accurate results and, therefore, we fixed its value at the lower theoretical limit. The pore volume v_p is fixed by the experimental values of the density and porosity of the experimental samples, which for the experimental data (Michels *et al.*, 2015) that we used were 2.8 gr/cm³ and 0.4, respectively. The remaining parameters, ϵ_{fs} and λ_i , were determined by fitting the calculated adsorption isotherm to the data.

The experimental data that we used were for excess CO₂ adsorption by a smectite clay (synthetic Li-fluorohectorite) sample at room temperature and pressures varying from 0 to 45 bars. The sample had a volume of 20 mm³, with a thickness of 1 mm. The elastic modulus and the Poisson's ratio of the material were taken to be, respectively, 2 GPa and 0.2 (although higher and lower values of the modulus have also been reported (Bathija, 2009; see below). Since the porous samples used in the experiments were thin, we used a 2D model whose microstructure, a random distribution of polygons representing the solid matrix in a uniform background, is shown in Figure 1. The effect of the microstructure is studied later (see below). The model's dimensions were selected such that they match those of the experimental sample and its porosity of 0.4 and, as pointed out earlier, periodic boundary conditions were used in the computations for the density field. The calculations with the FE method involved 2476 triangular element (see above). We checked that there is no finite-size effect by carrying out simulations with a larger system. The initial computations were carried out in order to determine the optimal values of the remaining two parameters. We obtained, $\epsilon^* = \epsilon_{fs}/\epsilon_{ff} \approx 1.38$ and $\lambda^* = \lambda_i/\epsilon_{ff} \approx -20$ for the dimensionless experimental temperature, $T^* = k_B T/\epsilon_{ff} \approx 0.73$. Unless specified otherwise, these are the values that we utilized in every case.

3.2 Sorption isotherms

Figure 2(a) presents a comparison between the computed isotherm and the experimental data, and the agreement is excellent. Both the experiments and the computed isotherm indicate that with increasing pressure, the excess adsorbed CO_2 increases smoothly to a maximum value, and then decreases at higher pressures. Figure 2(b) represents the corresponding absolute sorption isotherm, which reaches a plateau and remains unchanged at higher pressures.

Before studying various aspects of the model and its predictions, it is worth looking at the effect of the parameter λ_i on the isotherms. Recall that Eq. (6) represents the change in the elastic energy as a result of the presence of the adsorbed fluid with $\lambda_i \leq 0$. Thus, λ_i provides a link between the fluid adsorption and the solid deformation. When $\lambda_i = 0$, deformation of the solid is not affected by adsorption. Since a fit of the theoretical predictions to the data yielded, $\lambda^* \approx -20$, we also studied the case, $\lambda^* = 0$, holding all other parameters fixed.

In all the cases that we presented hereafter and the corresponding figures, the solid curves present the state of the dependent variable during adsorption, while the dashed curve indicate the same during desorption. Figure 3 presents the adsorption/desorption isotherms for two values, $\lambda^* = 0$ and -20 . The existence of a plateau in the sorption isotherm suggests, of course, that there is an optimal pressure for maximum storage of CO_2 . If $\lambda^* = 0$, i.e. when sorption does not affect solid swelling, sorption hysteresis is very weak, almost indiscernible. As the absolute value of λ^* increases, coupling deformation of the solid with adsorption, the fluid forces the solid to work harder in order to accommodate more fluid. Thus, hysteresis becomes stronger and more visible, because deformation changes the pore structure that is responsible for the hysteresis. The shape of the isotherms for the two cases are, however, identical, implying that the type of sorption isotherms and the pore-filling mechanism are not affected by the swelling. The deformation only assists more adsorption. The maximum amount of adsorbed fluid is higher when swelling and sorption are coupled.

Figure 4 presents the snapshots of the evolution of CO_2 density profile in the porous medium with increasing pressure for $\lambda^* = 0$, i.e. when sorption and deformation are decoupled. Darker areas correspond to higher amounts of adsorbed CO_2 . This should be compared with Figure 5 that presents the same evolution, but for the case, $\lambda^* = -20$. It is clear that the FE triangular elements that are neighbors to the solid skeleton of the porous medium are occupied

by CO₂ before the other sites, which once again demonstrates the mutual effects of sorption and deformation.

3.3 Sorption and deformation

Figure 6 presents the dependence of the total volumetric strain and the porosity of the system on the pressure. Due to the rigidity of the matrix the porosity increases by only about 3.4 percent over its original value, and even less when sorption is decoupled from deformation ($\lambda^* = 0$). This can also be understood by appealing to the variations of the total strain on the pressure, also shown in Figure 6. If we plot the strain versus the porosity, we obtain the results shown in Figure 7, indicating a linear relation between the two, which for small strains is expected and indicates that swelling is caused by gas adsorption (Heller and Zoback, 2014; see also Sahimi, 2011). The fact that the slope of the line is greater than one indicates that the matrix itself has swelled, contributing to the total strain (Kulasinski *et al.*, 2015a).

Figure 8 presents the swelling strain as a function of adsorbed amount of CO₂, indicating a linear relationship between the two. Although we do not have such data for the clay samples that we used for estimating the parameters of the model, we note that a linear relation between the strain and the adsorbed amount is in agreement with the experimental data for CO₂ adsorption in shales at low pressures (Lu *et al.*, 2016). Day *et al.* (2008) also reported that coal swelling and the amount of CO₂ adsorbed into it are linearly correlated for pressures less than 8 MPa. Hol *et al.* (2012; see also the theoretical work of Liu *et al.*, 2015) studied the volumetric strain in unconfined bituminous coal samples, exposed to adsorbing CO₂ at pressures up to 100 MPa and a temperature of 40°C. Their study also confirmed a linear relation between adsorption-induced swelling strain and the amount of adsorbed CO₂.

To better illuminate the effect of sorption on the strain and deformation of porous media, we computed the longitudinal and transverse strains, ϵ_x and ϵ_y , respectively. For example, the longitudinal strain ϵ_x , the change in the length of the matrix relative to its original length L_0 in the x direction (horizontal direction in Figure 1), is defined by

$$\epsilon_x = \frac{\Delta x}{L_0} . \quad (17)$$

A similar equation is used for ϵ_y . Figure 9 presents the two strains and their dependence on pressure and the parameter λ_i . We first note that strain changes anisotropically, the reason

for which is twofold. One is the deviation of the microstructure of the system from elastically-isotropic structures, such as hexagonal and triangular lattices. The second reason is due to the differences between the different elastic properties of the matrix and the fluid content of the pores. If we define a strain anisotropy by, $\mathcal{A} = \epsilon_y/\epsilon_x$, then its value at the maximum pressure $P = P_0$ is 1.4 for $\lambda^* = 0$, and 1.36 if $\lambda^* < 0$. Although we do not have any data for $\mathcal{A}$ for the experimental clay system with which we compare our results, our computed $\mathcal{A}$ is similar to the experimental data for CO₂ adsorption in shale samples for which the average anisotropy was reported to be 1.41 (Lu *et al.*, 2016). In addition, Figure 9 illustrates hysteresis in the strain as the porous medium first adsorbs CO₂ and then desorbs it. As with the sorption isotherms, the hysteresis is stronger when sorption is fully coupled with deformation of the solid matrix, since it is the structure of the material that gives rise to hysteresis, and swelling changes the microstructure.

3.4 Effect of the microstructure

It is of interest to study the effect of the microstructure of a porous medium on the sorption isotherms of CO₂ and the resulting swelling of the solid matrix. In particular, it is well-known that adsorption is not sensitive to pore interconnectivity, whereas desorption is, which is also why in many cases there is hysteresis between the two (Sahimi, 2011). Thus, we carried out a series of simulations with various microstructures. They included the cases in which the solid matrix was represented by square and triangular tiles, as well as the Voronoi polygons. We also considered the case in which the particle is represented by parallel pores sandwiched between platelets representing the solid matrix. All the microstructures are shown in Figure 10.

We first used the experimental data (Michels *et al.*, 2015) to fit the two parameters ϵ^* and λ^* for the Voronoi, triangular, square and parallel platelet microstructures. The results are listed in Table 1, and have a few notable features. (i) The parameters for the Voronoi and triangular structures are practically identical. The pore connectivity of the triangular network is six, as is the average connectivity of the pores in the Voronoi microstructure. Moreover, the values of the parameters for the random microstructure, which has a mean connectivity very close to 4, and those of the square microstructure are also identical. Thus, as long as the average connectivity of a disordered microstructure is the same as, or very close to, that of a regular one, the parameters of the model are essentially the same, an important result that was pointed out

long ago (Jerauld *et al.*, 1984a,b) in the context of conduction in disordered microstructures. (ii) The energy interaction parameter ϵ^* varies by greatly as the microstructure changes. Table 1 indicates that ϵ^* for the square microstructure is about 30 percent smaller than that of the parallel platelet microstructure, which has the highest value. (iii) The parameter λ^* exhibits stronger dependence on the microstructure than does ϵ^* , but it still varies by a factor less than 2. Such observations indicate the possibility of developing mean-field theories for estimating λ^* and ϵ^* , or computing them by MD simulations.

Figure 11 compares the sorption isotherms computed with the various microstructures. The difference between the various isotherms is mainly in the desorption isotherms. In particular, the hysteresis is most pronounced with the random and square microstructures that also happen to have the lowest connectivity. This is in line with what was pointed out earlier in that desorption and, hence, its hysteresis with adsorption are sensitive to the connectivity of a porous material. Since a pore cannot release the gas during desorption, unless it is connected to other pores that can do the same at the same pressure, hysteresis should be stronger in less connected microstructures. Note that the parallel platelets model exhibits no hysteresis, which is expected because the pores do not communicate with each other.

Figure 12 compares the pressure-dependence of the overall strain computed with the various microstructures. Similar to the sorption isotherms, the hysteresis between the strains build-up during adsorption and its release during desorption is most pronounced with the random and square microstructures. Moreover, Figure 12 indicates that the strain accumulation and release is far more sensitive to the connectivity than are the sorption isotherms. In agreement with Figure 11, the strain “isotherms” for the pairs of the microstructures that have similar connectivities are also close. Once again, the parallel platelets model does not exhibit any hysteresis.

Sorption isotherms have been used in the past in order to estimate the mean connectivity of porous materials (Seaton, 1991; Liu *et al.*, 1992). Since the pressure-dependence of strain manifests strong sensitivity to the connectivity, the implication is that one may be able to gain more information about the connectivity through mechanical measurements as a porous medium undergoes deformation during sorption.

3.5 Effect of the matrix rigidity

We also studied the effect of the rigidity of the solid matrix on deformation and sorption. Clearly, the more compliant the matrix, the more amenable it is to swelling during sorption. At the same time, the elastic moduli of clay materials vary over a relatively wide range, depending on their type and content (impurity). Thus, we carried out a series of simulations in which we assumed that the Young's modulus of the solid matrix was 0.15 GPa, which was reported for a clay-sand mixture and is more than ten times less than what we used in most of our calculations (Vallejo and Lobo-Guerrero, 2005). Also studied was the case in which the modulus was 10 GPa, five times larger than the base case.

The resulting pressure-dependence of the strain, its variations with the Young's modulus, and the comparison with the base case are shown in Figure 13. The significant feature of Figure 13 is that the hysteresis between the overall strain during adsorption and desorption decreases as the matrix becomes more rigid. This is understandable because when the matrix is more compliant, it is deformed more strongly. The deformation changes the structure of the matrix, which is the root cause of the hysteresis. Figure 14 presents the corresponding sorption isotherms. Similar to the strain, the hysteresis in the sorption isotherms is much stronger in the more compliant material. This is of course due to the strong deformation of the matrix that changes the pore space significantly, and in particular the pore connectivity, and hysteresis between adsorption and desorption is caused by the pores' interconnectivity. Moreover, the change in the rigidity also changes the amount of sorbed gas at low and intermediate pressures. As the matrix becomes more compliant, it requires less work to accommodate more fluids (see the earlier discussions), resulting in higher amounts of sorption at low and intermediate pressures.

Interestingly, if we fit the two parameters of the model, namely, λ^* and ϵ^* , to the experimental data (Michels *et al.*, 2015), assuming the lower or the higher values of the Young's modulus than the base case, we obtain, respectively, $\epsilon^* \approx 1.45$ and 1.38, which are practically identical with $\epsilon^* \approx 1.38$ that we obtained with the base case. This supports our contention that the interaction energy parameter between the fluid and the solid is essentially independent of the rigidity of solid matrix.

3.6 Effect of fluid-solid interaction

The interaction between a fluid and the solid is clearly one of the most important factors

in sorption in porous media. The same is true for sorption-induced deformation. Thus, it is of interest to study the effect of the interaction parameter ϵ_{fs} on the sorption isotherms and the change in the strain. The results for three values of $\epsilon^* = \epsilon_{fs}/\epsilon_{ff}$ are presented in Figure 15. The rest of the model’s parameters are the same as those of the baseline model, so that a direct comparison can be made. As ϵ^* decreases, the hysteresis loop becomes wider, because it is linked with the thermodynamic metastability that represents a system trapped in a local free-energy minimum (Gelb *et al.*, 1999). Qualitatively similar behavior and hysteresis loops are seen in the dependence of the overall strain on the pressure; see Figure 16.

The effect of temperature on sorption is well understood, and needs no explanation. As T increases, the amount of adsorbed gas decreases, implying that we should expect the overall, as well as the directional strains to also decrease because the swelling is due to sorption. Indeed, our model does predict this aspect correctly, which is also in agreement with the experimental studies on CO₂ sorption in shale and coal (Yang *et al.*, 2011; Lu *et al.*, 2016).

4. Possible Implications for Microseismic Events

In addition to their implications for storage of CO₂, deformation and swelling of porous media, such as rock, have two important consequences. One is the change that they induce in the mechanical properties of porous media by swelling. In a sense, the swelling causes the matrix to soften up, becoming more compliant (although some have disputed this; see, for example, Vandamme *et al.*, 2010; Hol *et al.*, 2011, 2012; Espinoza *et al.*, 2013). The second effect is associated with microseismic events (small earthquakes) triggered by deformation of porous media and rock that have been reported recently (Rothert and Shapiro, 2003; Maxwell *et al.*, 2008; Tafti *et al.*, 2013; Lee *et al.*, 2016).

The observed microseismic events may be triggered by one or both of the following mechanisms (see also Busch *et al.*, 2008). (i) The deformation and swelling of the matrix activate dormant fractures and cleavages that already reside in the matrix. Swelling might, of course, also produce an increase in the normal stress components that can just as well tend to close fractures and stabilize faults in a formation undergoing CO₂ uptake; see de Jong *et al.*, 2014. The activation of the fractures and cleavages triggers a microseismic event because deformation changes the stress field in rock, and may increase slip along the activated fractures. (ii) On the other hand, swelling softens up the matrix, making it more amenable to nucleation of new

fractures. This is particularly so when CO_2 is *injected* into the pore space, which builds up the pore pressure. Once new fractures have been nucleated, they may propagate and eventually trigger microseismic events.

It has been reported that such events do not usually occur at or very close to the injection point, but rather at a distance from it. This supports the hypothesis that microseismic events may be triggered by one or both of the aforementioned mechanisms, because either the dormant fractures closest to the injection point are first activated, leading to the activation of other dormant fractures at a distance from the injection, or new fractures must first be nucleated and propagated for some distance, changing the stress field and leading to a microseismic event. Both indicate that sorption (and flow that is not considered in this paper) of CO_2 may have profound effect on the structure of the geological formation in which it is to be stored. Thus, one must develop a comprehensive model that takes into account such effects, in order to better understand what happens to a geological formation when CO_2 is stored in it. Work in these directions is in progress.

5. Summary

This paper presented a model for deformation and swelling of porous media induced by their interaction with a fluid, and in particular its sorption. The model is based on the total energy (Hamiltonian) of the system that takes into account the interaction between the solid matrix of a porous medium and the adsorbing fluid, as well as the elastic energy stored in the material, and the interaction energy between the adsorbates themselves. The gas phase is described by a density functional theory. The model is capable of providing predictions for the sorption isotherms, the dependence of the strain on the pressure, as well as other properties of interest. The change in the strain is anisotropic due to the deformation of the solid matrix and the deviation of its underlying structure from two-dimensional elastically-isotropic materials, as well as the difference between the stiffness of the matrix and the bulk modulus of the fluid phase. As the adsorbed gas is desorbed, the strain is also released and, similar to the sorption isotherms, develops hysteresis with the strain increase during adsorption. This opens up the possibility of mechanical measurements during sorption experiments for deducing insight into the structure of the porous medium. When the model was applied to sorption of CO_2 in clay particles, all the reported experimental features of the phenomena were reproduced by

the model. The implications of the results for CO₂ storage in geological formations were also discussed, and future research directions were suggested.

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Table 1: Dependence of the parameters λ^* and ϵ^* on the microstructure.

	Random	Square	Triangular	Voronoi	Parallel Platelets
ϵ^*	1.38	1.38	1.65	1.65	1.98
λ^*	-20	-20	-12	-12	-20

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Figure 1: The microstructure of the system. The white areas represent where adsorption occurs, while the gray represents the solid skeleton. The triangles are due to finite-element discretization.

Figure 2: (a) Experimental data¹ (squares) and calculated (dashed line) excess adsorption isotherm at $T^* = 0.73$. (b) Calculated absolute adsorption isotherm at $T^* = 0.73$ for $\lambda^* = -20$ and $\epsilon^* = 1.38$.

Figure 3: CO_2 adsorption/desorption isotherms for $\epsilon^* = 1.38$ at $T^* = 0.73$.

Figure 4: Snapshots of CO_2 adsorption along the red isotherm in Figure 3 for $P/P_0 =$ (a) 0.12; (b) 0.14; (c) 0.26; (d) 0.35; (e) 0.56, and (f) 1.0, for $\lambda^* = 0$, $\epsilon^* = 1.38$, and $T^* = 0.73$. Darker regions represent higher densities of CO_2 .

Figure 5: Snapshots of CO_2 adsorption along the black isotherm in Figure 3 for $P/P_0 =$ (a) 0.12; (b) 0.14; (c) 0.26; (d) 0.35; (e) 0.56, and (f) 1.0, for $\lambda^* = -20$, $\epsilon^* = 1.38$, and $T^* = 0.73$. Darker regions indicate higher densities of CO_2 .

Figure 6: Dependence of (a) swelling strain, and (b) porosity on the pressure for $\epsilon^* = 1.38$ and $T^* = 0.73$.

Figure 7: Porosity-dependence of strain for $\epsilon^* = 1.38$ and $T^* = 0.73$.

Figure 8: Variation of strain with CO_2 density for $\lambda^* = -20$, $\epsilon^* = 1.38$, and $T^* = 0.73$.

Figure 9: Directional strains for $\epsilon^* = 1.38$ and $T^* = 0.73$.

Figure 10: The microstructures used in the simulations. (a) Triangular; (b) square; (c) Voronoi; (d) random pore space and (e) parallel platelets.

Figure 11: Adsorption/desorption isotherms computed with various microstructures and the parameters shown in Table 1 at temperature $T^* = 0.73$.

Figure 12: Dependence of the strain on the pressure computed with various microstructure and the parameters shown in Table 1 at temperature $T^* = 0.73$.

Figure 13: Dependence of the strain on the pressure and the Young's modulus Y of the matrix for $\lambda^* = -20$, $\epsilon^* = 1.38$, and $T^* = 0.73$.

Figure 14: Dependence of the adsorption/desorption isotherms on the Young's modulus Y of the solid, with $\lambda^* = -20$, $\epsilon^* = 1.38$, and $T^* = 0.73$.

Figure 15: Adsorption/desorption isotherms for $\lambda^* = -20$ and $T^* = 0.73$, and their dependence on the fluid-solid energy interaction parameter ϵ^* .

Figure 16: Dependence of the strain on the pressure P and the fluid-solid interaction parameter ϵ^* for $\lambda^* = -20$ and $T^* = 0.73$.