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Mechanics of adsorption–deformation coupling in porous media

Yida Zhang

Department of Civil, Environmental and Architectural Engineering, University of Colorado Boulder, Boulder, CO, USA

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ABSTRACT

This work extends Coussy's macroscale theory for porous materials interacting with adsorptive fluid mixtures. The solid-fluid interface is treated as an independent phase that obeys its own mass, momentum and energy balance laws. As a result, a surface strain energy term appears in the free energy balance equation of the solid phase, which further introduces the so-called adsorption stress in the constitutive equations of the porous skeleton. This establishes a fundamental link between the adsorption characteristics of the solid-fluid interface and the mechanical response of the porous media. The thermodynamic framework is quite general in that it recovers the coupled conduction laws, Gibbs isotherm and the Shuttleworth's equation for surface stress, and imposes no constraints on the magnitude of deformation and the functional form of the adsorption isotherms. A rich variety of coupling between adsorption and deformation is recovered as a result of combining different poroelastic models (isotropic vs. anisotropic, linear vs. nonlinear) and adsorption models (unary vs. mixture adsorption, uncoupled vs. stretch-dependent adsorption). These predictions are discussed against the backdrop of recent experimental data on coal swelling subjected to CO_2 and CO_2–CH_4 injections, showing the capability and versatility of the theory in capturing adsorption-induced deformation of porous materials.

1. Introduction

Classical poromechanics concerns the response of fluid-saturated porous media subjected to external forces and pore pressure changes. In the last decades, the original linear theory has been generalized for finite deformations (Biot, 1977; Gajo, 2010; Nedjar, 2013; Selvadurai and Suvorov, 2016), reformulated for analytical advantages (Anand, 2015; Rice and Cleary, 1976; Rudnicki, 1986), and extended for material inelasticity (Anand, 2017; Armero, 1999; Karrech et al., 2012). These theories belong to the so-called purely macroscale approaches in the sense that the constitutive responses are either defined a priori (e.g. Nur and Byerlee, 1971) or derived from a macroscopic Ψ-potential of the overall representative elementary volume (REV) (e.g. Biot, 1972; Coussy, 2004). Another approach follows the theory of mixtures (Atkin and Craine, 1976; Truesdell, 1962) in which the mixture is represented by spatially superposed interacting continua with the kinematics of each constituent described by Eulerian quantities. When specialized for porous media, one of the constituents is assigned as the solid phase and volume fractions are introduced to highlight the immiscibility between different phases (Bedford and Drumheller, 1983; Bowen, 1980; Pence, 2012). The constitutive relations of each constituent are derived from separate energy potentials and the macroscopic behaviour of the mixture is a result of averaging. Such formulation to certain extent reflects the microscale features of the porous media through the so-called *closure conditions* that govern the evolution of volume fraction of each constituent (de Boer, 1996). Candidates serving such condition include separate constitutive laws for volume

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E-mail address: yida.zhang@colorado.edu

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fractions (Kenyon, 1976), balance of equilibrated forces or balance of porosity (Nunziato and Cowin, 1979; Wilmanski, 1998), internal constraints enforced in the entropy inequality (de Boer, 1996; Svendsen and Hutter, 1995), and dynamic compatibility conditions on the interfaces (Wei and Muraleetharan, 2002). Readers shall refer to de Boer (2006) for a comprehensive survey. Mixture-based theories have been recently adapted for swelling and structural degradation of finitely strained polymers (Baek and Pence, 2009; Duda et al., 2010). Comparing the two approaches, mixture theories are more generic as they are derived from the fundamental balance laws of the system and can account for arbitrary number of constituents that could be miscible or immiscible and chemically inert or active. On the other hand, purely macroscale theories enjoy their straightforwardness and permit analytical solutions for important initial-boundary value problems related to engineering practices (e.g. Abousleiman and Cui, 1998; Cheng, 2016). Coussy (2004, 1998a) has shown that Biot's theory can be derived by reformulating the balance equations from mixture theories in terms of macroscopically measurable quantities, thus elucidating a profound connection between the two approaches. Specifically, the Lagrangian Clausius–Duhem inequality of the fluid-saturated porous media has been derived from the Eulerian balance equations of mass, momentum and energy of individual components. This inequality implies the existence of a single Ψ-potential that embodies the constitutive relations between the strain, fluid mass variation and temperature of the REV, which further leads to the usual thermoporoelasticity upon linearization. Such procedure has provided a thermodynamic foundation for Biot's theory and opened new avenues for the macroscale theories to benefit from the generality of mixture theories, i.e. to account for variably saturated conditions (Coussy, 2007), phase transitions (Coussy et al., 1998b) and chemical reactions (Coussy, 2010). The present study aims at continuing this line of development and formulating a purely macroscale theory for porous media immersed in adsorptive fluid mixtures.

The coupling between the adsorption/desorption of fluid molecules on pore surfaces and the deformation of porous solid has attracted growing research interest from physical chemistry, geological science, and energy industry (Cui and Bustin, 2005; Espinoza et al., 2014; Vandamme et al., 2010). One of the main drives is to understand and predict the swelling of coals during CO_2 sequestration, a process that changes the permeability of coal seams and impacts the efficiency of methane recovery. It has been observed that injecting CO_2 in methane-saturated coal seams can initially decrease the injectivity, followed by a permeability rebound as gas pressure increases (Palmer and Mansoori, 1996; Robertson, 2005). Experiments on unconfined coal samples have shown that the total strain increases monotonically with CO_2 pressure at low pressures (0–20 MPa) (George and Barakat, 2001; Levine, 1996), then decreases as the gas pressure keep increasing ($>$ 20 MPa) (Hol and Spiers, 2012). Similar coupling effect has been observed on other porous materials, e.g. porous glass (Scherer, 1986), metal-organic frameworks (Neimark et al., 2011), porous silicon (Dolino et al., 1996), silica aerogel (Reichenauer and Scherer, 2001) and zeolite (Sorenson et al., 2008). Early empirical models adopt Langmuir-like equations to link the swelling strain to gas pressure (Chikatamarla et al., 2004; Levine, 1996; Palmer and Mansoori, 1996). They cannot predict the contraction of coal at high pressures and are disconnected with the fundamental physical principles. Recent thermodynamic models emphasize the role of surface energy in adsorption/desorption induced swelling/ shrinkage of porous materials. They conceptualize surface tension of the solid-fluid interface as a "prestress" on the solid skeleton which causes some initial elastic strain even under apparently stress-free condition. Adsorption decreases the surface tension and consequently releases part of the elastic strain which appears as swelling of the porous solid. These models can quantitatively capture the evolution of strain and permeability during CO_2 pressurization (Li and Feng, 2016; Pan and Connell, 2007; Vandamme et al., 2010). The existence of a swelling-contraction transition point and the anisotropic swelling behaviour of coal specimens have also been predicted (Espinoza et al., 2013).

Despite their successes, the thermodynamic foundations of porous continua in adsorptive fluids have not been rigorously derived as done for the classical poromechanics theory by Coussy et al. (1998a), and no reference has been made to the balance laws established in mixture theories. This has created certain ambiguities. For example, many approaches rely on the following additive form of the free energy f_s (Li and Feng, 2016; Vandamme et al., 2010):

$$f_s(\varepsilon, \mathbf{e}, \phi) = \Psi_s(\varepsilon, \mathbf{e}, \phi) + u_{surf}(\varepsilon, \mathbf{e}, \phi) \tag{1}$$

where Ψ_s the Helmholtz free energy of the skeleton; u_{surf} is a new term account for energy storage in surface; ε the volumetric strain; $\mathbf{e}$ the strain deviator; ϕ the porosity. A consequence of such decomposition is that, an extra stress term called the *adsorption stress* σ_a appears as part of the work-conjugated stress of elastic strain (Coussy, 2010; Vandamme et al., 2010), through which the aforementioned prestress effect can be taken into account. However, the thermodynamic origin u_{surf} and its proper independent variables are not clear. According to Eq. (1), u_{surf} depends only on the kinematics of the skeleton (ε, $\mathbf{e}$, ϕ), assuming such energy can only be altered by mechanically stretching the interface $du_{surf} = \sigma^s dA_s$ where $A_s = A_s(\varepsilon, \mathbf{e}, \phi)$ is the specific surface area and σ^s is the surface stress. Then σ^s is made to depend on the chemical potential μ_i^f of the adsorbates to model adsorption-induced swelling. A consistency question naturally follows: should u_{surf} also depends on the states of the saturating fluid, thus having μ_i^f enters the arguments of u_{surf}? A further question is, is the additive structure of the free energy Eq. (1) merely a constitutive hypothesis, or is it rooted in the balance laws of the mixture? To answer these questions, it is necessary to revisit the thermodynamics of macroscale poromechanics and explicitly acknowledge solid-fluid interface in the system of interest.

The purpose of study is therefore two-fold: (1) to derive the balance laws for saturated adsorptive porous media that has surface as the third phase, hoping to justify the appearance of u_{surf} in Eq. (1) and clarify its independent variables; (2) to show the capability of this framework in modelling adsorption-induced swelling of porous materials against the backdrop of recent experimental results on CO_2 infiltrated coals. The paper is structured as follows: the mass, mole, momentum,