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Revisiting thermo-poro-mechanics under adsorption: Formulation without assuming Gibbs-Duhem equation

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Abstract

Gibbs-Duhem equation is a fundamental relation of the thermodynamics of fluids that originates from the extensive behavior of fluids. Fluids adsorption in micro-porous media can break the extensivity with respect to volume, so that Gibbs-Duhem equation does not hold in general for adsorbed fluid. As a consequence, a total of 6 moduli are needed to fully describe the thermo-mechanics of an adsorbed fluid instead of 3 for bulk fluids (compressibility, thermal expansion, and heat capacity). In recent years, poromechanics theory has been extended to capture the effects of fluid adsorption in micro-porous media, but the non-validity of Gibbs-Duhem equation has been disregarded so far. We propose here a new formulation of poromechanics extended to adsorption which does not assume Gibbs-Duhem equation. The introduction of 6 fluid moduli instead of 3 is a rather fundamental change that requires to revisit the derivation from the fundamentals of poromechanics. In addition, the new poromechanics is formulated to capture thermo-mechanical couplings in double porosity media (micro- and macro-pores) with potential fluid transfers between the porosities. The final constitutive equations exhibit the same structure as in usual poromechanics, but with effective poromechanical properties that are affected by fluid confinement. The impact of assuming Gibbs-Duhem equation or not is discussed. In particular, we show that relaxing the assumption of Gibbs-Duhem may explain some experimental observations of adsorption-induced effects that are not captured by existing poromechanics. The proposed theory should improve our understanding of micro-porous materials with wide perspectives for applications (clay, cement, wood, bones, microporous carbons etc.).

Keywords: poromechanics, adsorption, Gibbs-Duhem, micropores, drainage, couplings

1. Introduction

Gibbs-Duhem equation is one of the most important relation of the thermodynamics of fluids. It relates the changes of pressure (P), temperature (T) and chemical potential (μ) at equilibrium as follows:

$$VdP - SdT - Nd\mu = 0 \tag{1}$$

where V is the volume, S the entropy and N the number of molecules. Gibbs-Duhem equation originates from the extensive nature of the behavior of fluids, with respect to volume, number of particles and entropy. A classical derivation consists in considering the Gibbs free energy $G = U + PV - TS$ (with U the internal energy), which is the thermodynamic potential minimum at equilibrium for a system in thermal and mechanical equilibrium (T and P imposed). Because of extensivity, G depends linearly on the number of particles, and, by definition of the chemical potential $\mu = \partial G/\partial N|_{P,T}$, the Gibbs free energy of a fluid is

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simply $G = \mu N$. Combining this expression with the energy balance $dG = VdP - SdT + \mu dN$, one readily obtains Gibbs-Duhem equation (1).

Gibbs-Duhem equation has fundamental implications on the thermo-mechanical behavior of fluids. In particular, the fact that pressure, temperature and chemical potential are not independent, strongly constrains the behavior. Indeed, in the general case, a system of 3 state variables (N, V, S) has 3 independent conjugated variables (μ, P, T, respectively) and thus a minimum of 6 moduli are necessary to fully describe it (there are a total of 9 second derivatives of the internal energy, but only 6 are independent because of the Maxwell relations). Gibbs-Duhem equation, instead, implies that the 3 conjugated variables are no more independent, so that 3 additional relations constrain the moduli, and one is left with 3 independent moduli only, namely the compressibility, the thermal expansion and the heat capacity.

The applicability of Gibbs-Duhem equation to adsorbed fluids is questionable. Adsorption is the particular state of a fluid submitted to molecular interactions with a solid. Adsorption in porous solids becomes important as the size of the pores approaches a few nanometers or less, which is usually referred to as 'microporous' solids in contrast with 'macro-porous' solids in which most of the fluid is not adsorbed. Microporous solids are ubiquitous in natural environments and man-made structures (e.g., clay, wood, cement-based materials), and fluid adsorption in those materials is well known to induce unusual mechanical behavior such as swelling and drying shrinkage. The mechanical behavior of adsorbed fluids has attracted special attention in the recent years, thanks to the increasing accuracy of experimental techniques and of molecular simulation methods. In particular, it is now possible to estimate the so-called disjoining pressure, which is the difference between the pressure of an adsorbed fluid film and that of the same non-adsorbed fluid (bulk fluid) when the two fluids are in osmotic equilibrium. A key observation is that disjoining pressure varies with the thickness of the adsorbed film, at constant chemical potential and temperature (see the example of water in clay in Figure 1), which has been identified experimentally since the 1980's (Israelachvili, 1992). This observation contradicts Gibbs-Duhem equation, since it implies that pressure is not only a function of chemical potential and temperature, but also of the film thickness, that is of the volume of the fluid. Accordingly, one cannot apply Gibbs-Duhem equation to an adsorbed fluid, in the general case. And, as a consequence, up to 6 moduli are needed to fully describe the the thermo-mechanical behavior of an adsorbed fluid. For instance, in isothermal conditions, the pressure of a bulk fluid is a function of the density $\rho = N/V$ only, which is fully characterized by the rigidity (inverse of compressibility): $K = \rho \left.\frac{\partial P}{\partial \rho}\right|_T$. In other words, the dependencies of pressure on volume V and number of molecules N are strictly related: $K = -V \left.\frac{\partial P}{\partial V}\right|_{N,T} = N \left.\frac{\partial P}{\partial N}\right|_{V,T}$. For an adsorbed fluid, however, the pressure may exhibit unrelated dependencies in V and N, so that it is no more a function of density only (see the example of water in clay in Figure 1). Accordingly, one has to distinguish the rigidity associated to the volume $K^V = -V \left.\frac{\partial P}{\partial V}\right|_{N,T}$ from that associated to the number of particles $K^N = N \left.\frac{\partial P}{\partial N}\right|_{N,T}$.

The thermo-mechanical behavior of an adsorbed fluid is at the heart of the poro-mechanical behavior of microporous solids. In the literature, effects of fluid adsorption on mechanics have been investigated for a variety of microporous materials from zeolithes to metal organic frameworks and coal. The thermodynamics of it has been formulated by several with a variety of descriptions: surface adsorption versus micropore filling, formulations with or without the concept of pore volume, assuming a specific adsorption isotherm or not, single or double porosity medium (see for instance Murad and Cushman (2000); Ravikovitch and Neimark (2006); Kowalczyk et al. (2008); Coudert et al. (2008); Vandamme et al. (2010); Gor and Neimark (2010); Neimark et al. (2010); Pijaudier-Cabot et al. (2011); Brochard et al. (2012); Kulasinski et al. (2015); Zhang (2018)). Some of these approaches have been built on the framework of poromechanics (Coussy, 2010), which is particularly suitable for the study of materials under any complex conditions regarding drainage, heat transfer, and deformation (Murad and Cushman, 2000; Pan and Connell, 2007; Vandamme et al., 2010; Pijaudier-Cabot et al., 2011; Brochard et al., 2012; Nikoosokhan et al., 2012; Vermorel and Pijaudier-Cabot, 2014; Nikoosokhan et al., 2014; Perrier et al., 2015, 2018; Zhang, 2018). A common point between all poromechanical formulations is that the adsorbed fluid exerts a pressure on the solid that differs from the pressure of a bulk fluid. Many existing poromechanical models were applied to amorphous materials (e.g., coal or activated carbons), for which the amount of fluid adsorbed n follows the very peculiar scaling

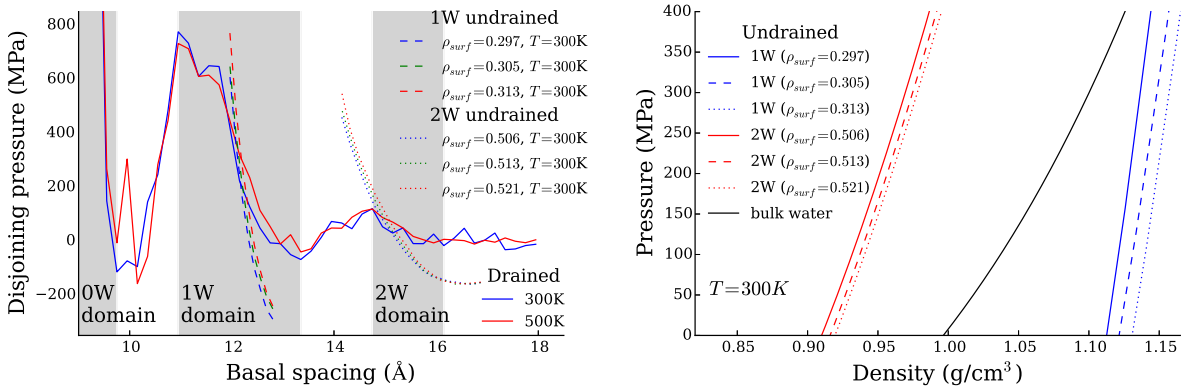

Figure 1: Mechanical behavior of confined water in Na-Montmorillonite in drained and undrained conditions obtained by molecular simulation (Honorio et al., 2017). (left) Drained behavior characterized by the disjoining pressure isotherm in function of the basal spacing. The shaded domains correspond to the stable basal spacings (decreasing branches of the disjoining pressure isotherm), referred to as xW with x the number of water layers in the micropore. Dashed and dotted curves are the undrained behavior for the 1W and 2W states, respectively. (right) Undrained pressure-density curves for the 1W and 2W states of water at different amount of surface density ρ_{surf} (amount of water per unit area, in unit of mg/m^2). Because of adsorption, pressure is no more a function of density only, as in the case of bulk water.

$n \approx n_0\,(P,T)\,(1+C\epsilon)$, with C a constant analogous to the inverse of a porosity (Brochard et al., 2012). This scaling is similar to assuming a density of the adsorbed fluid in the microporosity independent of the volume of micropores (Pijaudier-Cabot et al., 2011; Vermorel and Pijaudier-Cabot, 2014), that is assuming an extensive behavior and the validity of Gibbs-Duhem equation. Studies dedicated to non-amorphous media such as clays (Murad and Cushman, 2000) do recognize the effect of pore size on fluid pressure, but still assume fluid density as an appropriate state parameter of the confined fluid (Murad and Cushman (2000) restrict themselves to large micropores, $\sim$ 10 water layers, for which they reasonably assume the same density for the bulk and adsorbed water). This leads to a modified Gibbs-Duhem equation which imposes constraints on the thermo-mechanical moduli. Accordingly, the validity of Gibbs-Duhem equation for confined fluids has not been questioned so far.

To address this limitation, in this work, we propose a new formulation of poromechanics under adsorption which relaxes the assumption of Gibbs-Duhem equation. Relaxing Gibbs-Duhem is a fundamental change since one has to introduce 3 new moduli characterizing the thermo mechanics of the adsorbed fluid. These original developments offer a more general description of microporous materials than existing theories, opening new perspectives for a better understanding of the mecano-sorption processes in microporous materials in general. In addition, the new poromechanics is formulated to include thermo-mechanical couplings in a double porosity medium (micro- and macro-pores), which contributes to the originality of this work since most existing poromechanics under adsorption are limited to isothermal formulations for single porosity media.

In section 2, we recall the usual thermo-mechanical description of a bulk fluid, and we formulate the description of an adsorbed fluid, i.e., without assuming Gibbs-Duhem equation. In section 3, we recall the derivation of usual non-linear thermo-poro-mechanics. In section 4, we revisit this derivation to account for the new description of an adsorbed fluid. In section 5, we extend this new formulation to a double porosity medium with both micro-pores (adsorbed fluid) and macro-pores (bulk fluid). Finally, in section 6, we discuss the implications of this work for the understanding of mecano-sorption phenomena. The detailed derivation of the new poromechanics is sometimes lengthy and, in the paper, we limit ourselves to a synthetic presentation (particularly in sections 4 and 5). A full step-by-step derivation is provided in supporting information. For sake of clarity, the notations and structure of the new poromechanics are chosen to reflect the notations and structure of usual poromechanics. In particular, we adopt a systematic ordering of constitutive equations to make it easy to check the thermodynamic consistency (Maxwell relations).

Moreover, the notations of effective tangent properties in the extended poromechanics use the same symbols as in usual poromechanics with a superscript $\square^{eff}$ for the extension to microporous media, and a tilde plus a superscript $\tilde{\square}^{eff}$ for the extension to micro-macro-porous media.

2. Fluid behavior

The thermodynamic state of a pure component fluid is described by three state parameters (e.g., volume V, number of particles N and temperature T) and the behavior is given by the three constitutive equations relating the conjugated variables (pressure P, chemical potential μ and entropy S) to the state parameters, i.e., 9 tangent properties (e.g., $\frac{\partial P}{\partial V}\big|_{N,T}$ etc.). Because of the 3 Maxwell relations (e.g., $\frac{\partial P}{\partial N}\big|_{V,T} = -\frac{\partial \mu}{\partial V}\Big|_{N,T}$ etc.), only 6 of these tangent properties are independent. In the particular case of a bulk fluid, Gibbs-Duhem relation ($VdP - Nd\mu - SdT = 0$) imposes 3 additional relations between these properties. Accordingly, for bulk fluids, one is left with 3 thermodynamical properties that are enough to fully describe the thermo-mechanical behavior: the bulk modulus K (inverse of compressibility), the thermal expansion α, and the volumetric heat capacity $c^v = \frac{T}{V}\frac{\partial S}{\partial T}\big|_{N,V}$. With these properties, the constitutive equations for a bulk fluid for the state parameters (V_b, N_b, T) are (see supporting information):

$$\begin{cases} dP_b = -K_b \frac{dV_b}{V_b} + K_b \frac{dN_b}{N_b} + K_b \alpha_b dT \\ d\mu = -\frac{K_b}{N_b} dV_b + \frac{K_b V_b}{N_b^2} dN_b - \left(\frac{S_b}{N_b} - K_b \frac{V_b}{N_b}\alpha_b\right) dT \\ dS_b = K_b \alpha_b dV_b + \left(\frac{S_b}{N_b} - K_b \frac{V_b}{N_b}\alpha_b\right) dN_b + V_b c_b^v \frac{dT}{T} \end{cases} \tag{2}$$

where the subscript $_b$ refers to the 'bulk fluid'. In the above formulation, we do not use the subscript $_b$ for the chemical potential μ and the temperature T because in all what follows we assume osmotic equilibrium between the adsorbed and bulk fluids (i.e., they share the same μ and T).

The Gibbs-Duhem relation arises because the Gibbs free energy of a bulk fluid is extensive with respect to the number of particles of the fluid. But this is no more the case in general for adsorbed fluids since confinement breaks the extensivity with respect to volume. As a consequence, the proper thermodynamic description of the fluid requires 6 independent properties. A possible set of such properties is the following (other set are possible which would be equally valid):

1. the drained bulk modulus $K^d = -V\ \frac{\partial P}{\partial V}\big|_{\mu,T}$
2. the undrained bulk modulus $K^V = -V\ \frac{\partial P}{\partial V}\big|_{N,T}$
3. the rigidity with respect to the number of particles at constant volume and temperature $K^N = -N\ \frac{\partial P}{\partial N}\big|_{V,T}$
4. the drained thermal expansion $\alpha^d = \frac{1}{V}\ \frac{\partial V}{\partial T}\big|_{P,P_b}$
5. the undrained thermal expansion $\alpha^u = \frac{1}{V}\ \frac{\partial V}{\partial T}\big|_{N,P}$
6. the volumetric heat capacity c^v

The constitutive equations for a confined fluid for the state parameters (V_c, N_c, T) are (see supporting information):

$$\begin{cases} dP_c = & -K_c^V \frac{dV_c}{V_c} + K_c^N \frac{dN_c}{N_c} + K_c^V \alpha_c^u dT \\ d\mu = & -\frac{K_c^N}{N_c} dV_c + \frac{\left(K_c^N\right)^2}{K_c^N - K_c^d}\frac{V_c}{N_c^2} dN_c - \left(\frac{S_b}{N_b} + \frac{K_c^N}{K_c^N - K_c^d}\frac{V_c}{N_c}\left(K_c^d \alpha_c^d - K_c^V \alpha_c^u\right)\right) dT \\ dS_c = & K_c^V \alpha_c^u dV_c + \left(\frac{S_b}{N_b} + \frac{K_c^N}{K_c^N - K_c^d}\frac{V_c}{N_c}\left(K_c^d \alpha_c^d - K_c^V \alpha_c^u\right)\right) dN_c + \frac{V_c c_c^v}{T} dT \end{cases} \tag{3}$$

where the subscript $_c$ refers to the 'confined fluid'. In the following of the paper, we prefer using the term 'confined' rather than 'adsorbed' since we are interested in fluids confined in micropores whereas adsorption often refers to solid surfaces. In Equations (3), one of the coupling terms involves the entropy per particle in the bulk fluid (S_b/N_b), that is the entropy per particle of the same fluid in the bulk state at same chemical

potential and temperature. This term originates from the use of the Gibbs-Duhem relation for a bulk fluid in osmotic equilibrium with the confined fluid, because the definition of the drained thermal expansion α^d is at constant pressure of a reservoir fluid (bulk), and not at constant chemical potential.

The case of a bulk fluid is recovered for $K^V = K^N$, $K^d = 0$ and $\rho_c = \rho_b$ with $\rho = N/V$ the number density. For sake of readability, we introduce the following notations: $K_c = K_c^N$, $\gamma = 1 - \frac{K_c^d}{K_c^N}$, $\delta = \frac{K_c^V}{K_c^N}$, and $\alpha_c^{eff} = \frac{\delta}{\gamma}\alpha_c^u - \frac{1-\gamma}{\gamma}\alpha_c^d$. We thus obtain a formulation of the constitutive equations close to that of a bulk fluid, in which all the peculiarity of the confined fluid is captured in the deviations of γ, δ, and ρ_c/ρ_b from 1:

$$\begin{cases} dP_c = -\delta K_c \frac{dV_c}{V_c} + K_c \frac{dN_c}{N_c} + \delta K_c \alpha_c^u dT \\ d\mu = -\frac{K_c}{N_c} dV_c + \frac{1}{\gamma}\frac{K_c V_c}{N_c^2} dN_c - \left(\frac{S_b}{N_b} - K_c \frac{V_c}{N_c}\alpha_c^{eff}\right) dT \\ dS_c = \delta K_c \alpha_c^u dV_c + \left(\frac{S_b}{N_b} - K_c \frac{V_c}{N_c}\alpha_c^{eff}\right) dN_c + \frac{V_c c_c^v}{T} dT \end{cases} \tag{4}$$

In the above constitutive behavior, we implicitly assume that one can define a volume of the confined fluid. The concept of volume at the scale of nanometric pores is questionable. Some existing formulations of poromechanics extended to adsorption do not require to introduce any micropore volume (Brochard et al., 2012). Indeed, in the appropriate thermodynamic ensemble, introducing porosity is not necessary and one only needs to know the amount of fluid in the pores. In such a formulation, one considers the porous medium as a whole and does not distinguish between the fluid and the solid contributions in the adsorption-induced pressure: the fluid generates a pore pressure while the solid skeleton responds by deforming the porosity until thermodynamic equilibrium is reached. Yet, these approaches are not easily transferable to thermo-poro-mechanics because one would need to know the excess entropy due to adsorption, for which no usual model exists and estimation is complex (thermodynamic integration). Alternatively, in the present work, we do introduce a micropore volume and distinguish between fluid and solid contributions. This approach is more in line with the usual framework of thermo-poro-mechanics (poromechnical moduli are combinations of solid and fluid moduli, no thermodynamic integration needed). Introducing a micropore volume necessarily comes with a degree of arbitrariness. For some microporous materials, defining a micropores size is easy (periodic crystals: MOFs or zeolithes, slit or cylindrical pores: clays or nanotubes). For other materials (amorphous carbons, polymers), no clear definite pore size can be identified. The current theory is directly applicable to microporous materials with definite pore sizes. For materials with non-definite pore sizes, the present theory can be adapted with a mean field approach. This is left for future developments.

3. Usual poromechanics

Once the behavior of the fluid is set, one can address the behavior of a porous medium saturated with this fluid. This is the purpose of the established theory of usual poromechanics (Coussy, 2010) which assumes that the fluid filling the porosity is in its bulk state. The thermodynamic equilibrium of a porous medium at controlled strain ($\underline{\underline{\varepsilon}}$), pore pressure ($P$) and temperature ($T$) is obtained by minimization of an appropriate thermodynamic potential $\eta_s = f_s - \phi P$ which is a Legendre transform of the Helmholtz free energy per unit undeformed volume f_s, with ϕ the Lagrangian porosity. The first derivatives of η_s provide the conjugated quantities: stress $\underline{\underline{\sigma}} = \left.\frac{\partial \eta_s}{\partial \underline{\underline{\varepsilon}}}\right|_{P,T}$, porosity $\phi = \left.\frac{\partial \eta_s}{\partial P}\right|_{\underline{\underline{\varepsilon}},T}$, and entropy of the solid skeleton per unit undeformed volume $s_s = \left.\frac{\partial \eta_s}{\partial T}\right|_{\underline{\underline{\varepsilon}},P}$. This is summarized in the energy balance :

$$d\eta_s = \underline{\underline{\sigma}} : d\underline{\underline{\varepsilon}} - \phi dP - s_s dT \tag{5}$$

From now on, we disregard the deviatoric behavior of the medium, which is generally assumed uncoupled with the fluid (Coussy, 2010), and limit ourselves to the spherical behavior only (spherical stress $\sigma = tr\left(\underline{\underline{\sigma}}\right)/3$ conjugated to the volumetric strain $\epsilon = tr\left(\underline{\underline{\varepsilon}}\right)$ so that the contribution to the energy balance is $\sigma d\epsilon$). The constitutive thermo-poro-mechanical behavior of the porous medium is given by the expressions of stress,

porosity and entropy as a function of strain, pressure and temperature. In the framework of non linear elasticity, we have the following incremental formulation (Coussy, 2010):

$$\begin{cases} d\sigma = Kd\epsilon - bdP - K\alpha dT \\ d\phi = bd\epsilon + \frac{dP}{N} - \alpha_\phi dT \\ ds_s = K\alpha d\epsilon - \alpha_\phi dP + \frac{c}{T}dT \end{cases} \tag{6}$$

where:

- K is called the bulk modulus of the medium,
- b the Biot coefficient,
- N the Biot modulus,
- α the thermal expansion of the porous medium,
- α_ϕ the pore thermal expansion,
- and c the heat capacity of the porous medium.

All these properties depend on the porous solid behavior only and verify (for a homogeneous solid skeleton):

$$b = 1 - \frac{K}{k_s},\ \frac{1}{N} = \frac{b-\phi}{k_s},\ \alpha = \alpha_s,\ \alpha_\phi = \alpha_s\left(b-\phi\right), \text{ and } c = c_s\left(1-\phi\right) - KT\alpha_s^2 \tag{7}$$

where k_s, α_s, and c_s are the bulk modulus, thermal expansion, and volumetric heat capacity of the solid skeleton, respectively.

Therefore, in usual poromechanics, the drained properties are independent of the fluid. The undrained properties, however, strongly depend on the behavior of the fluid, since any porosity change induces pressurization of the pore fluid. In undrained conditions, the appropriate thermodynamic potential to consider is the Helmholtz free energy of the porous medium (solid and bulk fluid) $f = f_s + f_b$ for which the energy balance is (see supporting information):

$$df = \sigma d\epsilon + \mu d\left(\phi\rho_b\right) - sdT \tag{8}$$

where μ and ρ_b are the chemical potential and number density of the fluid, respectively, and s is the total entropy (solid plus fluid) per unit undeformed volume. Therefore, in undrained conditions the thermodynamic property conjugated to the amount of fluid $\phi\rho_b$ is the chemical potential of the fluid μ. Combining the drained behavior (Eqs. 6) and the bulk fluid behavior (Eqs. 2), we obtain the following constitutive equations of the undrained behavior (see supporting information):

$$\begin{cases} d\sigma = K_u d\epsilon - \frac{Mb}{\rho_b} d\left(\phi\rho_b\right) - K_u\alpha_u dT \\ d\mu = -\frac{Mb}{\rho_b} d\epsilon + \frac{M}{\rho_b^2} d\left(\phi\rho_b\right) + \frac{M\alpha_\mu}{\rho_b} dT \\ ds = K_u\alpha_u d\epsilon - \frac{M\alpha_\mu}{\rho_b} d\left(\phi\rho_b\right) + \frac{c_u}{T} dT \end{cases} \tag{9}$$

where:

- $\frac{1}{M} = \frac{1}{N} + \frac{\phi}{K_b}$ is the undrained Biot modulus,
- $K_u = K + Mb^2$ is the undrained bulk modulus,
- $K_u\alpha_u = K\alpha_s + Mb\alpha_{\rho\phi}$ is the undrained thermal rigidity,
- $M\alpha_\mu = M\alpha_{\rho\phi} - s_b$ is the undrained thermo-chemical coupling coefficient,
- and $\frac{c_u}{T} = \frac{c+\phi c_b^v}{T} + \frac{K_b}{\phi}\left(\phi\alpha_b\right)^2 - M\alpha_{\rho\phi}^2$ is the undrained heat capacity,
- with $\alpha_{\rho\phi} = \alpha_\phi + \phi\alpha_b$ the thermal expansion of the fluid-solid mixture.

4. Poromechanics extended to confined fluids

In this section, we revisit the derivation of usual poromechanics in the context a confined fluid filling the pores. The usual formulation of poromechanics (Eqs. 6) assumes that one can control the pressure P exerted by the fluid on the solid. This is not true for a microporous material because the pressure within the pores differs from the bulk pressure of the 'outside' fluid (i.e., what an experimentalist actually controls). Since the porous medium is an open system with respect to the fluid, the pore fluid and the outside fluid can exchange particles and, accordingly, osmotic equilibrium requires equality of their chemical potentials. Therefore, for a microporous medium under drained conditions, the valid control parameter is no more the pressure of the fluid P, but the chemical potential μ. This change of paradigm means that the appropriate thermodynamic potential to consider is no more η_s but $\omega = f - \mu\phi\rho_c$ (see supplementary information) with f the Helmholtz free energy of the porous medium (solid and fluid) and ρ_c the confined fluid density within the pores (i.e., $\phi\rho_c$ is the number of fluid particle in the pores per unit undeformed volume). In the corresponding energy balance, the quantity conjugated to the fluid chemical potential is the amount of fluid $\phi\rho_c$ and the quantity conjugated to the temperature is the total entropy s of the porous medium (fluid and solid):

$$d\omega = \sigma d\epsilon - \phi\rho_c d\mu - sdT \tag{10}$$

According to Gibbs-Duhem equation, controlling μ and T is equivalent to controlling P_b (bulk) and T, and the energy balance of ω can be rewritten:

$$d\omega = \sigma d\epsilon - \phi^{eff} dP_b - s^{eff} dT \tag{11}$$

with $\phi^{eff} = \frac{\phi\rho_c}{\rho_b}$ an effective (apparent) porosity (ρ_c is the density of the confined fluid, ρ_b is that of the bulk fluid at same chemical potential and temperature), and $s^{eff} = s - \phi^{eff} s_b$ an effective entropy (s_b is the entropy per unit volume of the bulk fluid at same chemical potential and temperature). Comparing the energy balances (5) and (11), it appears that the bulk pressure of the (outside) fluid is no more conjugated to the porosity ϕ but to the effective porosity ϕ^{eff}. Likewise, the temperature is no more conjugated to the entropy of the solid skeleton $s_s = s - \phi s_b$ but to the effective entropy $s^{eff} = s - \phi^{eff} s_b$. For consistency, one can easily check that $\phi^{eff} \to \phi$ in the limit of a bulk fluid in the pores, so that the energy balance of ω and η_s are identical in the limit of a macro-porous solid.

Combining the constitutive equations of the solid skeleton (Eqs. 6) and of the bulk and confined fluids (Eqs. 2 and 4), we obtain the following constitutive behavior of the drained microporous medium (see supplementary information):

$$\begin{cases} d\sigma = K^{eff} d\epsilon - b^{eff} dP_b - K^{eff}\alpha^{eff} dT \\ d\phi^{eff} = b^{eff} d\epsilon + \frac{dP_b}{N^{eff}} - \alpha_\phi^{eff} dT \\ ds^{eff} = K^{eff}\alpha^{eff} d\epsilon - \alpha_\phi^{eff} dP_b + \frac{c^{eff}}{T} dT \end{cases} \tag{12}$$

where:

- $K^{eff} = K + M^d b^2$ is the effective bulk modulus,
- $b^{eff} = \frac{\beta b \delta \rho_c}{\rho_b}$ is the effective Biot coefficient,
- $K^{eff}\alpha^{eff} = K^{eff}\alpha_s + M^d b\phi \left(\frac{1-\gamma}{\delta-\gamma}\alpha_c^d - \alpha_s\right)$ is the effective thermal rigidity,
- $\frac{1}{N^{eff}} = \phi^{eff}\left(\gamma\frac{1-\beta}{\delta-\gamma}\frac{\delta\rho_c}{\rho_b}\frac{1}{K_c} - \frac{1}{K_b}\right)$ is the effective Biot modulus,
- $\alpha_\phi^{eff} = \alpha\left(b^{eff} - \delta\beta\phi^{eff}\right) + \phi^{eff}\left(\delta\alpha_c^u - \delta\left(1-\beta\right)\frac{1-\gamma}{\delta-\gamma}\alpha_c^d - \alpha_b\right)$ is the effective pore thermal expansion,
- and $\frac{c^{eff}}{T} = \frac{c + \phi c_c^v - \phi^{eff} c_b^v}{T} + \phi\delta K_c\left(\alpha_c^u\right)^2 - \phi^{eff} K_b\left(\alpha_b\right)^2 + \frac{\delta-\gamma}{\gamma}\phi\delta K_c\left(\alpha_c^u - \frac{1-\gamma}{\delta-\gamma}\alpha_c^d\right)^2 - M^d\left(\alpha_\phi + \phi\frac{1-\gamma}{\delta-\gamma}\alpha_c^d\right)^2$ is the effective heat capacity;

- with $\frac{1}{M^d} = \frac{1}{N} + \frac{1}{\delta-\gamma}\frac{\phi}{K_c}$ a coefficient analogous to an undrained Biot modulus due to fluid confinement, and $\beta = \frac{\gamma}{\delta-\gamma}\frac{\phi M^d}{\delta K_c}$.

According to these effective poromechanical properties, the behavior of the confined fluid does impact the properties of the drained porous medium, whereas in usual poromechanics, the drained poromechanical properties depend on the solid only. Thus, fluid confinement can induced unusual behaviors, one of the most well-known being adsorption induced swelling and contraction. This generalized formulation is consistent with usual poromechanics since, in the limit of a bulk fluid filling the pores ($\gamma \to 1$, $\delta \to 1$ and $\rho_c \to \rho_b$), we have $M^d \to 0$, $\beta \to 1$, and $\rho_c \to \rho_b$ so that all effective properties recover their usual values.

Let us now consider the undrained behavior. As in usual poromechanics, the appropriate thermodynamic potential to consider is the Helmholtz free energy, with the following energy balance:

$$df = \sigma d\epsilon + \mu d\left(\phi\rho_c\right) - sdT \tag{13}$$

The quantity conjugated to the amount of fluid ($\phi\rho_c$) is the chemical potential. Combining the behavior of the solid skeleton (Eqs. 6) and that of the confined fluid (Eqs. 4) one can derive the behavior of the undrained porous medium (see supplementary information):

$$\begin{cases} d\sigma = K_u^{eff} d\epsilon - \frac{M^{eff} b^{eff}}{\rho_b} d\left(\phi\rho_c\right) - K_u^{eff}\alpha_u^{eff} dT \\ d\mu = -\frac{M^{eff} b^{eff}}{\rho_b} d\epsilon + \frac{M^{eff}}{\rho_b^2} d\left(\phi\rho_c\right) + \frac{M^{eff}\alpha_\mu^{eff}}{\rho_b} dT \\ ds = K_u^{eff}\alpha_u^{eff} d\epsilon - \frac{M^{eff}\alpha_\mu^{eff}}{\rho_b} d\left(\phi\rho_c\right) + \frac{c_u^{eff}}{T} dT \end{cases} \tag{14}$$

where:

- $M^{eff} = \frac{\mathcal{M}^{eff}}{\beta}\left(\frac{\rho_b}{\delta\rho_c}\right)^2$ is the effective undrained Biot modulus,
- $K_u^{eff} = K^{eff} + M^{eff}\left(b^{eff}\right)^2$ is the effective undrained bulk modulus,
- $K_u^{eff}\alpha_u^{eff} = K\alpha + \frac{M^{eff} b^{eff}}{\beta}\alpha_{\rho\phi}^{eff}$ is the effective undrained thermal rigidity,
- $\alpha_\mu^{eff} = \alpha_{\rho\phi}^{eff} + \delta\left(1-\beta\right)\phi^{eff}\left(\alpha_c^u - \frac{1-\gamma}{\delta-\gamma}\alpha_c^d\right) - \frac{s_b}{\rho_b}$ is the effective undrained thermo-chemical coupling coefficient,
- and $\frac{c_u^{eff}}{T} = \frac{c+\phi c_c^v}{T} + \frac{\delta K_c}{\phi}\left(\phi\alpha_c^u\right)^2 - \frac{M^{eff}}{\beta}\left(\alpha_{\rho\phi}^{eff}\right)^2$ is the effective undrained heat capacity;
- with $\alpha_{\rho\phi}^{eff} = \beta\frac{\delta\rho_c}{\rho_b}\left(\alpha_\phi + \phi\alpha_c^u\right)$ the effective thermal expansion of the fluid-solid mixture and $\frac{1}{\mathcal{M}^{eff}} = \frac{1}{N} + \frac{\phi}{\delta K_c}$.

5. Double porosity medium with macro- and micro-porosities

The effects of confinement and adsorption are limited to micropores ($\sim$ nm). But in many applications, the porosity is also made of larger pores, which we refer to as macropores. Since the fluid pressure differs between macropores (bulk fluid) and micropores (confined fluid), a proper poromechanical description of these materials must distinguish micro- and macro-porosities. In this section, we propose a double porosity thermo-poro-mechanics adapted to micro-macro-porous media. The detailed derivation, rather cumbersome, is given in supplementary information. We recall here the main steps only.

In usual double porosity poromechanics (Coussy, 2010), one considers a porous solid with a first macro-porosity ϕ_b submitted to a pressure P_b, and a second micro-porosity ϕ_c submitted to a pressure P_c. At controlled strain ϵ, pressures P_b and P_c, and temperature T, the thermodynamic potential minimum at equilibrium is $\eta_s = f_s - \phi_b P_b - \phi_c P_c$ and the corresponding energy balance is $d\eta_s = \sigma d\epsilon - \phi_b dP_b - \phi_c dP_c - s_s dT$. The constitutive behavior of the porous solid is given by (Coussy, 2010):

$$\begin{cases} d\sigma = Kd\epsilon - b_b dP_b - b_c dP_c - K\alpha dT \\ d\phi_b = b_b d\epsilon + \frac{dP_b}{N_{bb}} + \frac{dP_c}{N_{bc}} - \alpha_{\phi_b} dT \\ d\phi_c = b_c d\epsilon + \frac{dP_b}{N_{bc}} + \frac{dP_c}{N_{cc}} - \alpha_{\phi_c} dT \\ ds_s = K\alpha d\epsilon - \alpha_{\phi_b} dP_b - \alpha_{\phi_c} dP_c + \frac{c}{T} dT \end{cases} \tag{15}$$

where:

- K, α, and c are the bulk modulus, thermal expansion and volumetric heat capacity as for a single porosity solid;
- b_b, N_{bb}, α_{ϕ_b}, b_c, N_{cc}, and α_{ϕ_c} are the Biot coefficients and moduli and thermal expansions of the macro- and micro-pores, respectively;
- and N_{bc} is the Biot modulus characterizing the mechanical coupling between the two porosities.

All the moduli in this constitutive behavior are properties of the porous solid only. For a homogeneous solid skeleton with bulk modulus k_s, thermal expansion α_s, and volumetric heat capacity at constant stress c_s, the poromechanical properties verify (Coussy, 2010):

$$b_b + b_c = 1 - \frac{K}{k_s},\ \frac{1}{N_{ii}} + \frac{1}{N_{bc}} = \frac{b_i - \phi_i}{k_s},\ \alpha = \alpha_s,\ \alpha_{\phi_i} = \alpha_s \left(b_i - \phi_i\right), \text{ and } c = c_s \left(1 - \phi_b - \phi_c\right) - KT\alpha_s^2 \tag{16}$$

The constitutive equations (15) describe an unconnected porous medium in which the pore pressures P_b and P_c are independent. When the pores are connected, the two fluids can exchange particles so that, at equilibrium, they share the same chemical potential μ. In drained conditions, the appropriate control parameter is therefore μ instead of P_b and P_c. The thermodynamic potential minimum at equilibrium is a Legendre transform of the Helmholtz free energy of the porous medium (solid and fluid): $\omega = f - \mu\left(\phi_b\rho_b + \phi_c\rho_c\right)$; and the corresponding energy balance $d\omega = \sigma d\epsilon - \left(\phi_b\rho_b + \phi_c\rho_c\right) d\mu - sdT$ points to the total amount of fluid $(\phi\rho)_{tot} = \phi_b\rho_b + \phi_c\rho_c$ as to the quantity conjugated to the chemical potential μ. Because of Gibbs-Duhem equation (which holds for the macroporosity), controlling μ and T is equivalent to controlling P_b and T. Thus, one can rewrite the energy balance as follows: $d\omega = \sigma d\epsilon - \tilde{\phi}_{eff} dP_b - \tilde{s}_{eff} dT$ where $\tilde{\phi}_{eff} = \phi_b + \phi_c \frac{\rho_c}{\rho_b}$ is an effective porosity conjugated to the bulk fluid pressure, and $\tilde{s}_{eff} = s - \tilde{\phi}_{eff} s_b$ is an effective entropy conjugated to the temperature. The constitutive behavior of the drained connected porous medium can be derived from that of the unconnected medium (Eqs. 15) and of the fluids (Eqs. 2 for the bulk fluid $_b$ and Eqs. 4 for the confined fluid $_c$) (see supplementary information). We recover a constitutive behavior with a structure analogous to that of a single porosity medium:

$$\begin{cases} d\sigma = \tilde{K}^{eff} d\epsilon - \tilde{b}^{eff} dP_b - \tilde{K}^{eff} \tilde{\alpha}^{eff} dT \\ d\tilde{\phi}^{eff} = \tilde{b}^{eff} d\epsilon + \frac{dP_b}{\tilde{N}^{eff}} - \tilde{\alpha}_{\phi}^{eff} dT \\ d\tilde{s}^{eff} = \tilde{K}^{eff} \tilde{\alpha}^{eff} d\epsilon - \tilde{\alpha}_{\phi}^{eff} dP_b + \frac{\tilde{c}^{eff}}{T} dT \end{cases} \tag{17}$$

where:

- $\tilde{K}^{eff} = K + \tilde{M}^d b_c^2$ is the effective bulk modulus,
- $\tilde{b}^{eff} = b_b + \tilde{\beta} \frac{\delta\rho_c}{\rho_b} b_c$ is the effective Biot coefficient,
- $\frac{1}{\tilde{N}^{eff}} = \frac{1}{N_{bb}} - \frac{1}{\tilde{M}^d} \left(\frac{\tilde{\beta}\delta\rho_c}{\rho_b}\right)^2 + \phi_c^{eff} \left(\frac{\delta\gamma}{\delta-\gamma} \frac{\rho_c}{\rho_b} \frac{1}{K_c} - \frac{1}{K_b}\right)$ is the effective Biot modulus,
- $\tilde{K}^{eff} \tilde{\alpha}^{eff} = \tilde{K}^{eff} \alpha + \tilde{M}^d b_c \phi_c \left(\frac{1-\gamma}{\delta-\gamma} \alpha_c^d - \alpha\right)$ is the effective thermal rigidity,
- $\tilde{\alpha}_{\phi}^{eff} = \alpha_s \left(\tilde{b}^{eff} - \left(\phi_b + \delta\tilde{\beta}\phi_c^{eff}\right)\right) + \phi_c^{eff} \left(\delta\alpha_c^u - \alpha_b + \delta\left(1 - \tilde{\beta}\right) \frac{1-\gamma}{\delta-\gamma} \alpha_c^d\right)$ is the effective pore thermal expansion,

- and $\frac{\tilde{c}^{eff}}{T} = \frac{c+\phi_c c_c^v - \phi_c^{eff} c_b^v}{T} + \phi_c \delta K_c \left(\alpha_c^u\right)^2 - \phi_c^{eff} K_b \left(\alpha_b\right)^2 + \frac{\delta-\gamma}{\gamma} \phi_c \delta K_c \left(\alpha_c^u - \frac{1-\gamma}{\delta-\gamma}\alpha_c^d\right)^2 - \tilde{M}^d \left(\alpha_{\phi_c} + \phi_c \frac{1-\gamma}{\delta-\gamma}\alpha_c^d\right)^2$ is the effective heat capacity;
- with $\phi_c^{eff} = \phi_c \frac{\rho_c}{\rho_b}$, $\frac{1}{\tilde{M}^d} = \frac{1}{N_{cc}} + \frac{1}{\delta-\gamma}\frac{\phi_c}{K_c}$, and $\tilde{\beta} = \tilde{M}^d \left(\frac{\gamma}{\delta-\gamma}\frac{\phi_c}{\delta K_c} - \frac{\rho_b}{\delta \rho_c}\frac{1}{N_{bc}}\right)$.

The case of a single porosity medium is recovered as a particular case of double porosity medium with one of the porosities that vanishes ($\phi_i = b_i = \frac{1}{N_{ii}} = \frac{1}{N_{bc}} = 0$).

The undrained behavior of the connected porous medium is then easily obtained from the drained behavior by rearranging the constitutive equations. At controlled total amount of fluid $(\phi\rho)_{tot}$, the conjugate quantity is the chemical potential μ (following the balance of Helmholtz free energy $df = \sigma d\epsilon + \mu d\left(\phi\rho\right)_{tot} - sdT$). We have:

$$\begin{cases} d\sigma = \tilde{K'}_u^{eff} d\epsilon - \frac{\tilde{M}^{eff}\tilde{b}^{eff}}{\rho_b} d\left(\phi\rho\right)_{tot} - \tilde{K'}_u^{eff} \tilde{\alpha'}_u^{eff} dT \\ d\mu = -\frac{\tilde{M}^{eff}\tilde{b}^{eff}}{\rho_b} d\epsilon + \frac{\tilde{M}^{eff}}{\rho_b^2} d\left(\phi\rho\right)_{tot} + \frac{\tilde{M}^{eff}\tilde{\alpha'}_\mu^{eff}}{\rho_b} dT \\ ds = \tilde{K'}_u^{eff} \tilde{\alpha'}_u^{eff} d\epsilon - \frac{\tilde{M}^{eff}\tilde{\alpha'}_\mu^{eff}}{\rho_b} d\left(\phi\rho\right)_{tot} + \frac{\tilde{c'}_u^{eff}}{T} dT \end{cases} \tag{18}$$

where:

- $\frac{1}{\tilde{M}^{eff}} = \frac{1}{\tilde{N}^{eff}} + \frac{\tilde{\phi}^{eff}}{K_b}$ is the effective undrained Biot modulus,
- $\tilde{K'}_u^{eff} = \tilde{K}^{eff} + \tilde{M}^{eff}\left(\tilde{b}^{eff}\right)^2$ is the effective undrained bulk modulus,
- $\tilde{K'}_u^{eff} \tilde{\alpha'}_u^{eff} = \tilde{K}^{eff}\tilde{\alpha}^{eff} + \tilde{M}^{eff}\tilde{b}^{eff}\left(\tilde{\alpha}_{\rho\phi}^{eff} + \delta\left(1-\tilde{\beta}\right)\phi_c^{eff}\left(\alpha_c^u - \frac{1-\gamma}{\delta-\gamma}\alpha_c^d\right)\right)$ is the effective undrained thermal rigidity,
- $\tilde{\alpha'}_\mu^{eff} = \tilde{\alpha}_{\rho\phi}^{eff} + \delta\left(1-\tilde{\beta}\right)\phi_c^{eff}\left(\alpha_c^u - \frac{1-\gamma}{\delta-\gamma}\alpha_c^d\right) - \frac{s_b}{\rho_b}$ is the effective undrained thermo-chemical coupling coefficient,
- $\frac{\tilde{c'}_u^{eff}}{T}$ is the effective undrained heat capacity (see expression in supplementary information);
- with $\tilde{\alpha}_{\rho\phi}^{eff} = \left(\alpha_{\phi_b} + \phi_b\alpha_b\right) + \tilde{\beta}\frac{\delta\rho_c}{\rho_b}\left(\alpha_{\phi_c} + \phi_c\alpha_c^u\right)$ the effective thermal expansion of the fluid-solid mixture.

As for the drained behavior, one can verify that the case of a single porosity medium is recovered in the limit when one of the porosities vanishes.

6. Discussion

In presence of fluid confinement, all poro-mechanical moduli become effective since they involve the confined fluid properties (K_c, α_c^u, α_c^d, δ, γ, c_c^v, and ρ_c). The usual relations of poromechanics (Eq. 7) do not hold for these effective properties. And the usual restrictions such as $K > 0$, $N > 0$ or $0 < b < 1$ are no more required. Instead, there are different restrictions: thermodynamic stability requires the definite positiveness of the Hessian matrix of the internal energy, which imposes in particular $K^{eff} > 0$, $N^{eff} > 0$ or $c^{eff} > 0$. Thus K and N do not have to be positive anymore as soon as it is compensated by the confined fluid behavior so that $K^{eff} > 0$ and $N^{eff} > 0$. The effective Biot coefficient b^{eff} is not limited by 0 or 1, and values outside this range are indeed reported in the literature (Cariou et al., 2012; Honorio et al., 2018; Honorio, 2019). The fact that the usual restrictions of poromechanics do not apply for microporous media, opens the door to uncommon mechanical behavior that would be forbidden in usual poromechanics. We discuss hereafter a few of those anomalous behaviors.

In the new formulation of poromechanics, considering Gibbs-Duhem equation not valid is the most fundamental change with respect to existing literature. Assuming Gibbs-Duhem equation valid imposes 3 constraints on the fluid properties: $K^V = K^N$ (same rigidity with respect to volume and number of

molecules), $K^d = 0$ (no drained rigidity) and $K^d\alpha^d = 0$ (no drained thermal rigidity). With our choice of notations, this translates into $\delta = 1$, $\gamma = 1$ and $(1-\gamma)\,\alpha^d = 0$, so that the effects of confinement and adsorption on the thermo-poro-mechanics (Eqs. 12) would be the consequence of the ratio of densities ρ_c/ρ_b only. A confined density higher than the bulk density would lead to a confined pressure higher than the bulk pressure and conversely. We discuss hereafter the implication of assuming Gibbs-Duhem or not for three practical situations: deformation in isothermal unjacketed conditions, thermal expansion in drained conditions, and fluid thermal pressurization in undrained conditions.

The most well-known adsorption-induced effect is the swelling/shrinkage in isothermal ($dT = 0$), unjacketed ($\sigma = -P_b$) conditions (Gor et al., 2017). According to the usual and extended poromechanics (Eqs. 6 and 12), the incremental deformation upon an increase of bulk fluid pressure takes the form:

$$\left.\frac{\partial \epsilon}{\partial P_b}\right|_{\sigma=-P_b,T} = \begin{cases} -\frac{1-b}{K} = -\frac{1}{k_s} \text{ usual poromechanics} \\ -\frac{1-b\frac{\rho_c}{\rho_b}}{K} \text{ ext. poromech. with G-D} \\ -\frac{1-b\frac{\beta\delta\rho_c}{\rho_b}}{K+M^d b^2} \text{ ext. poromech. without G-D} \end{cases} \tag{19}$$

According to usual poromechanics, a porous medium in unjacketed conditions should exhibit a slight shrinkage corresponding to the compressibility of the solid skeleton. According to extended poromechanics assuming Gibbs-Duhem, one should observe a swelling if $\rho_c/\rho_b > 1/b$ and a shrinkage if $\rho_c/\rho_b < 1/b$. In particular, in the case of adsorption of a vapor, one expects a very high ratio ρ_c/ρ_b (density of the confined fluid similar to that of a liquid) and so an induced swelling. Yet, this is not systematically the case in experiments, in particular at low vapor pressure (Gor et al., 2017). Instead, extended poromechanics without assuming Gibbs-Duhem has not the same restriction, since the term involving the ratio ρ_c/ρ_b is modulated by β which can take any value. Therefore, relaxing Gibbs-Duhem assumption may explain why vapor adsorption sometimes lead to contraction.

A second situation of interest is the thermal expansion of the medium in drained conditions. According to the usual and extended poromechanics, we have:

$$\left.\frac{\partial \epsilon}{\partial T}\right|_{\sigma,P_b} = \begin{cases} \alpha_s \text{ usual poromechanics} \\ \alpha_s \text{ ext. poromech. with G-D} \\ \alpha_s + \frac{M^d b\phi}{K+M^d b^2}\left(\frac{1-\gamma}{\delta-\gamma}\alpha_c^d - \alpha_s\right) \quad \begin{array}{l}\text{ext. poromech.}\\ \text{without G-D}\end{array} \end{cases} \tag{20}$$

Accordingly, extended poromechanics assuming Gibbs-Duhem predicts the same expansion as usual poromechanics: α_s. Thermal expansion of solids are usually around 10^{-5} K^{-1}, but micro-porous solids can exhibit much larger expansions. For instance the thermal expansion of over-consolidated clays (i.e., clays with reversible mechanical behavior) can reach 10^{-4} K^{-1} (Sultan et al., 2002), which is in a range comparable to the thermal expansion of liquid water. Such a large expansion is attributed to confined water, but this phenomenon is not captured by extended poromechanics assuming Gibbs-Duhem. In contrast, extended poromechanics without assuming Gibbs-Duhem leads to a more complex expression of the thermal expansion, which involves the drained thermal expansion of the confined fluid, presumably much larger than the thermal expansion of the solid skeleton. Therefore, relaxing Gibbs-Duhem may explain this high thermal expansion, whereas assuming Gibbs-Duhem clearly contradicts the observation.

A last situation of interest is the case of heating in undrained conditions under constant confining stress. Since the fluid usually exhibits a much higher thermal expansion than the solid, one usually expects a pressurization of the fluids (note that the measured pressurization is that of the outside bulk fluid P_b, not that inside the micropores P_c). According to the usual and extended poromechanics in undrained conditions (Eqs. 9 and 14), we have :

$$\left.\frac{\partial P_b}{\partial T}\right|_{\sigma,\phi\rho} = \begin{cases} \frac{KM\phi}{K_u}\left(\alpha_b - \alpha_s\right) \text{ usual poromechanics} \\ \frac{\rho_b}{\rho_c}\frac{KM\phi}{K_u}\left(\alpha_c^u - \alpha_s\right) \text{ ext. poromech. with G-D} \\ \left(\begin{array}{c} \frac{\rho_b}{\delta\rho_c}\frac{K\mathcal{M}^{eff}\phi}{K_u^{eff}}\left(\alpha_c^u - \alpha\right) \\ +\frac{\rho_b}{\rho_c}\frac{\delta-\gamma}{\gamma}K_c\left(\alpha_c^u - \frac{1-\gamma}{\delta-\gamma}\alpha_c^d\right) \end{array}\right) \begin{array}{c} \text{ext. poromech.} \\ \text{without G-D} \end{array} \end{cases} \tag{21}$$

In the case of clay, Monfared et al. (2011) have shown that the pressurization predicted by usual poromechanics underestimates experimental measurements by 30 to 50%. Extended poromechanics assuming Gibbs-Duhem leads to an expression of thermal pressurization identical to that of usual poromechanics, but with the ratio of densities $\frac{\rho_b}{\rho_c}$ as prefactor. The experiments of Monfared et al. (2011) are performed in saturated conditions (i.e., the bulk fluid is liquid water), so that the ratio $\frac{\rho_b}{\rho_c}$ is expected to be close to 1. Therefore, extended poromechanics assuming Gibbs-Duhem is not expected to give a better prediction than usual poromechanics for the thermal pressurization of water in undrained clays. Instead, extended poromechanics without assuming Gibbs-Duhem leads to a quite different expression of pressurization with two contributions. One can interpret the different contributions as a combination of partial derivatives as follows:

$$\left.\frac{\partial P_b}{\partial T}\right|_{\sigma,\phi\rho_c} = \underbrace{\frac{\rho_b}{\delta\rho_c}}_{\left.\frac{\partial P_b}{\partial P_c}\right|_{T,\phi\rho_c}} \underbrace{\frac{K\mathcal{M}^{eff}}{K_u^{eff}}\phi\left(\alpha_c^u - \alpha\right)}_{\left.\frac{\partial P_c}{\partial T}\right|_{\sigma,\phi\rho_c}} + \underbrace{\frac{\rho_b}{\rho_c}\frac{\delta-\gamma}{\gamma}K_c\left(\alpha_c^u - \frac{1-\gamma}{\delta-\gamma}\alpha_c^d\right)}_{\left.\frac{\partial P_b}{\partial T}\right|_{P_c,\phi\rho_c}} \tag{22}$$

The first contribution is similar to the expression of usual poromechanics. It combines the increase of bulk fluid pressure due to the increase of confined pressure, and the increase of confined pressure due to undrained heating. The second contribution is much less intuitive, primarily because it does not depend on the porous solid moduli or even on the porosity. Carefully analyzing the confined fluid behavior (Eq. 4), one can interpret this term as the increase of bulk pressure with temperature at constant confined pressure and amount of fluid. This contribution arises from a mismatch between the thermal expansion at constant bulk pressure and at constant confined pressure : $\frac{\delta-\gamma}{\gamma}\left(\alpha_c^u - \frac{1-\gamma}{\delta-\gamma}\alpha_c^d\right) = \frac{1}{V_c}\left.\frac{\partial V_c}{\partial T}\right|_{P_b,\phi\rho_c} - \frac{1}{V_c}\left.\frac{\partial V_c}{\partial T}\right|_{P_c,\phi\rho_c}$. This contribution to thermal pressurization is intrinsic to the confined fluid and holds irrespective of the poromechanical properties of the solid or of the porosity. Most importantly, this contribution arises only if Gibbs-Duhem equation is not assumed for the confined fluid. This new contribution may explain the anomalously high thermal pressurization of water in clays.

7. Conclusion

In this work, we propose a new formulation of non-linear thermo-poro-mechanics extended to the effects of adsorption. The development of this formulation is motivated by the observation that Gibbs-Duhem equation does not hold in general for adsorbed fluids. Gibbs-Duhem equation, which originates from the extensive behavior of fluids, is a fundamental relation that limits the thermo-mechanical description of a fluid to 3 moduli (compressibility, thermal expansion, and heat capacity). Considering Gibbs-Duhem not valid implies that the description of a confined fluid relies on 6 moduli instead of 3. This is a fundamental change that requires to revisit the derivation of poromechanics from the fundamentals of thermodynamics. In addition, this new poromechanics has been formulated to account for thermo-mechanical couplings and for double porosity media (micro- and macro-pores), which adds to the originality of the formulation since existing formulation of poromechanics extended to adsorption are all limited to isothermal conditions and most consider single porosity media only.

The final constitutive equations of the extended thermo-poro-mechanics are given by Equations (12) and (14) for the drained and undrained single porosity medium, respectively, and by Equations (17) and (18) for the drained and undrained double porosity medium, respectively. These constitutive behaviors involve effective poromechanical properties (bulk modulus, Biot coefficient, thermal expansion etc...) that extend the usual ones to the effect of the confined fluid. This opens new perspectives for a better understanding of

the mechanical behavior of microporous materials in general with various applications from clay-rich soils to industrial adsorbents.

We show that considering Gibbs-Duhem valid or not has important implications regarding the predicted adsorption-induced effects, which could explain some experimental observation that are not captured by existing poromechanical formulations. The expressions of adsorption-induced effects involve all 6 fluid moduli except the heat capacity. A difficulty, though, for practical quantitative applications, is to have estimates of those moduli. Such an estimation is challenging since experimental measurement of adsorbed fluid properties requires nanometric precision. One can also perform inverse analysis based on effective properties of microporous solids, but it remains a challenge to disentangle 6 moduli by inverse analysis. A convenient alternative to experiment is molecular simulation. Recent advances in molecular simulation techniques provide reasonable estimates of confined fluid properties at the nanoscale. Application of the new poromechanics with such estimates of the confined fluid moduli will be the focus of future works.

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