Addressing bound water in the thermo-poro-mechanical modeling of swelling clays

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October 10th, 2024
Comité Français de Mécanique des Roches

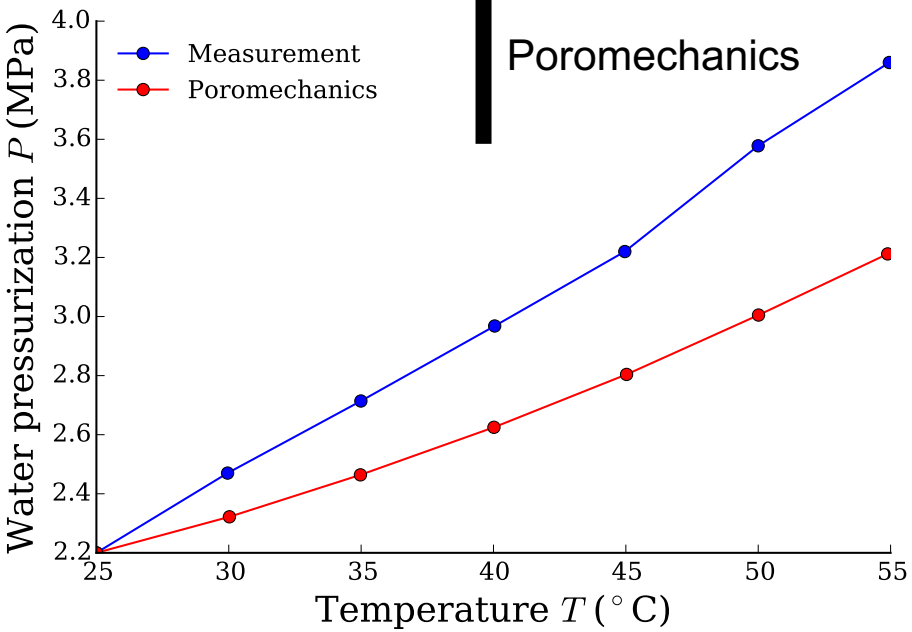
1st anomaly: undrained heating experiment

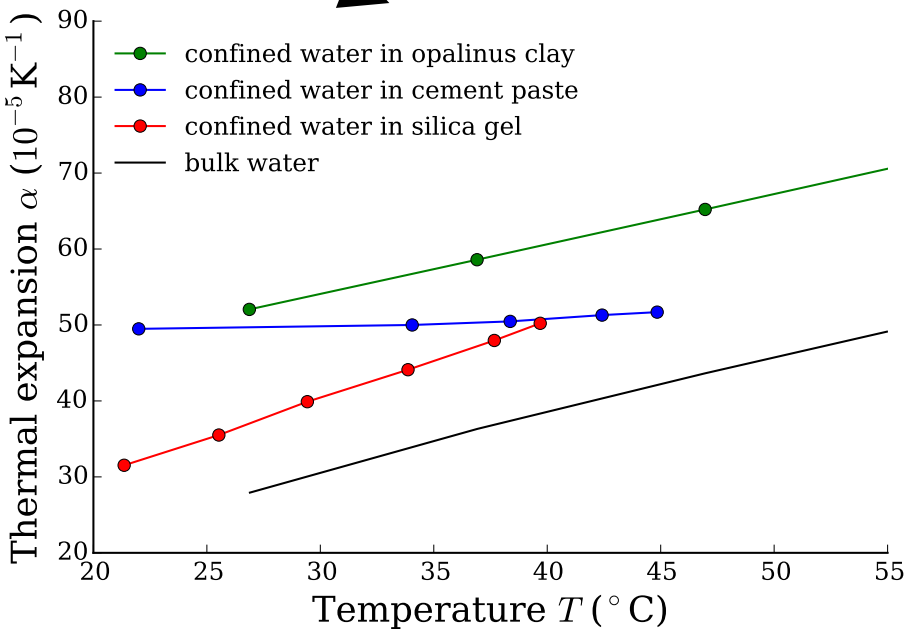
- Excessive water pressurization

$$\left.\frac{\partial P_b}{\partial T}\right|_{\sigma,\phi\rho_b} = \frac{KM\phi}{K_u}\left(\alpha_b - \alpha_s\right)$$

Interpretation:
bound water thermal expansion
higher than bulk water th. exp.

Poromechanics

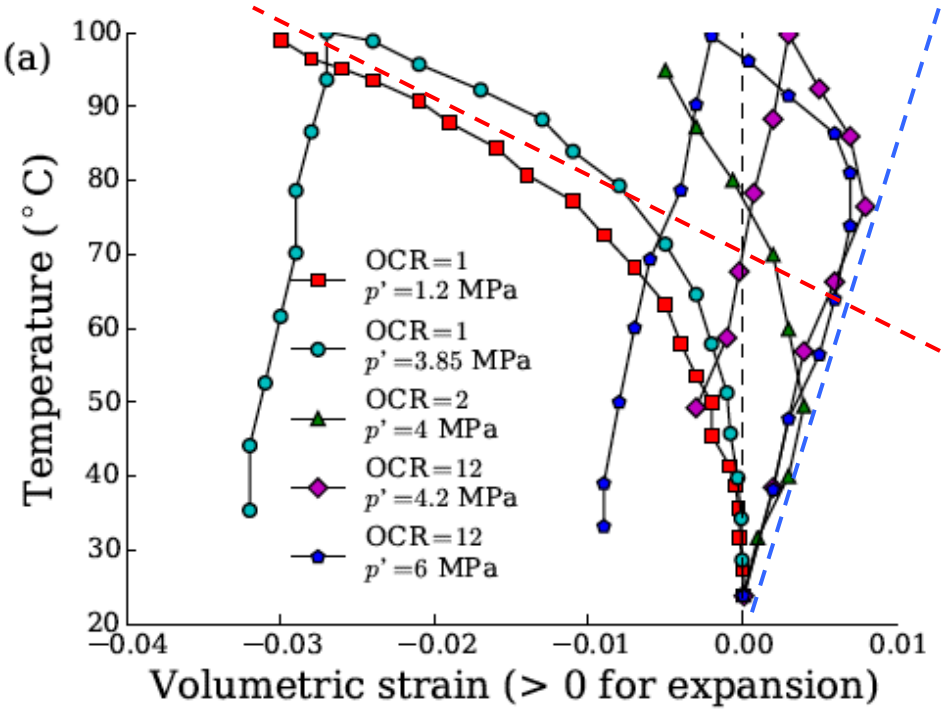




Monfared, M., Sulem, J., Delage, P., & Mohajerani, M. (2011). A Laboratory Investigation on Thermal Properties of the Opalinus Claystone. Rock Mechanics and Rock Engineering, 44(6), 735–747. http://doi.org/10.1007/s00603-011-0171-4

2nd anomaly: drained heating experiment

- Reversible thermal expansion excessive
- Irreversible contraction (normally consolidated clays)



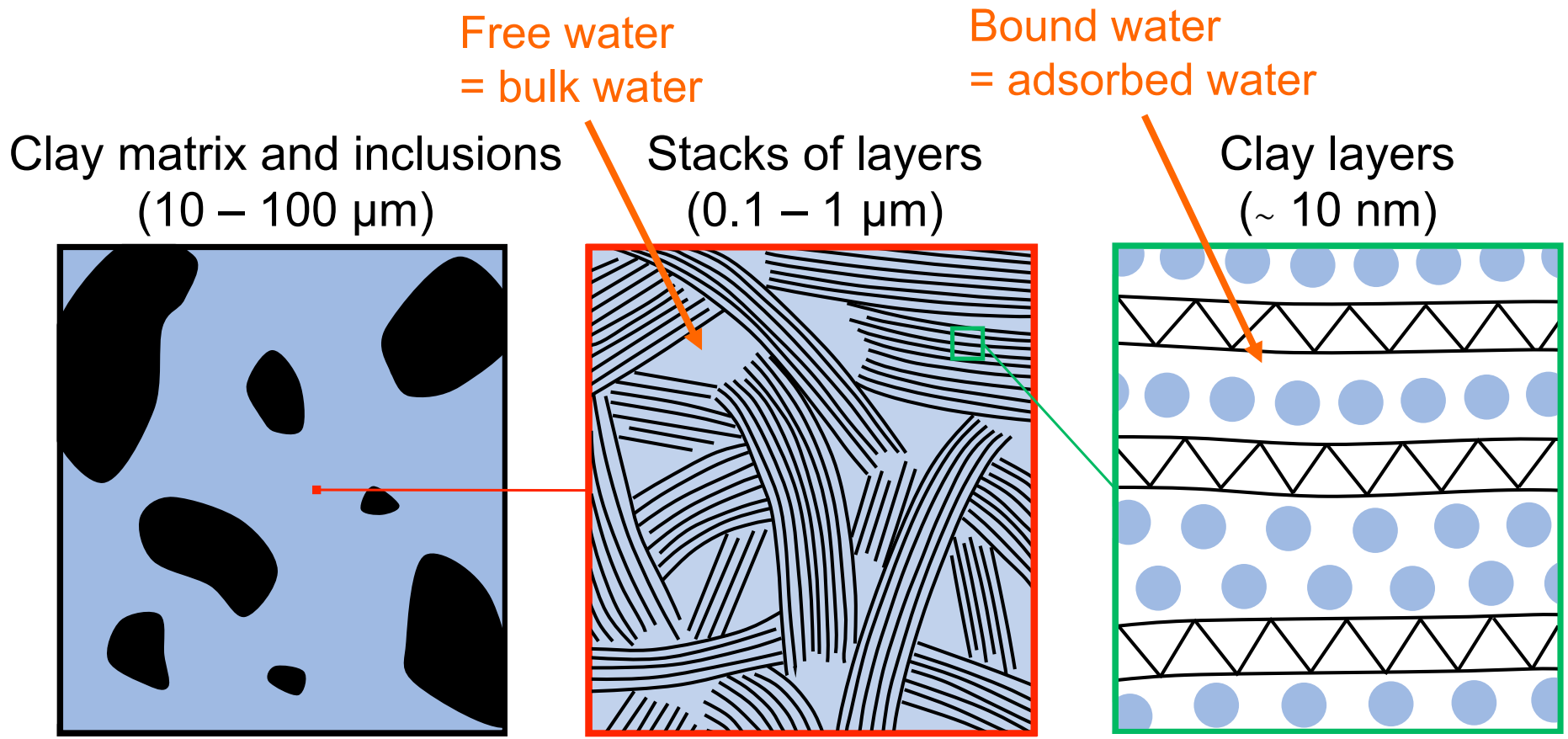
$\alpha_{reversible}$ ~ 10^{-4} K^{-1}
$\alpha_{minerals}$ ~ 10^{-5} K^{-1}
Interpretation:
bound water is not drained

$\alpha_{irreversible}$ ~ -10^{-3} K^{-1}
Interpretation:
drainage of bound water

Sultan, N., Delage, P., & Cui, Y. J. (2002). Temperature effects on the volume change behaviour of Boom clay. Engineering Geology, 64(2-3), 135–145. http://doi.org/10.1016/S0013-7952(01)00143-0

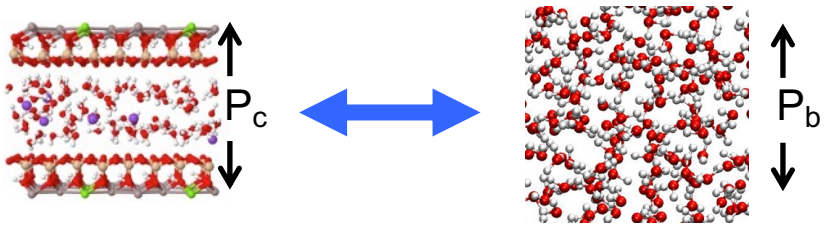
Objective: poromechanics capturing adsorption

- Anomalies attributed to the effects of adsorption
- Usual poromechanics assumes bulk properties



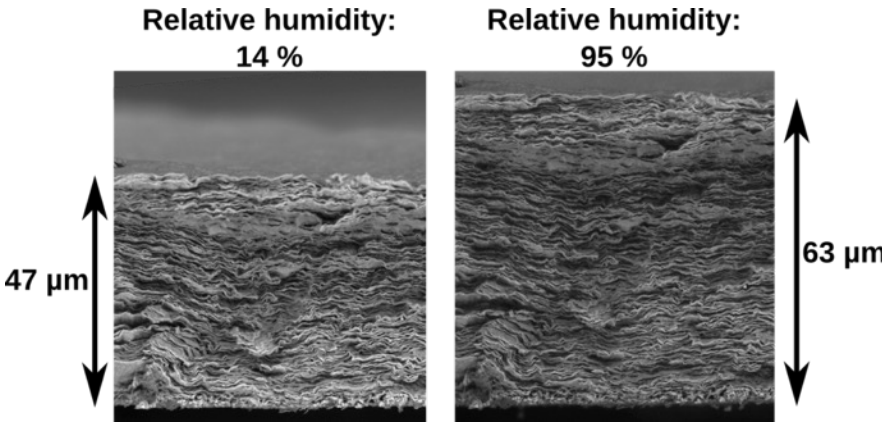
Poromechanics and adsorption

- Thermodynamic description : osmotic equilibrium between adsorbed and bulk phases



- Effect on mechanics:
  - Disjoining pressure $P_c \neq P_b$
  - P_c is affected by composition or temperature independently from P_b

→ Ex: swelling effect due to P_c at P_b = Cst

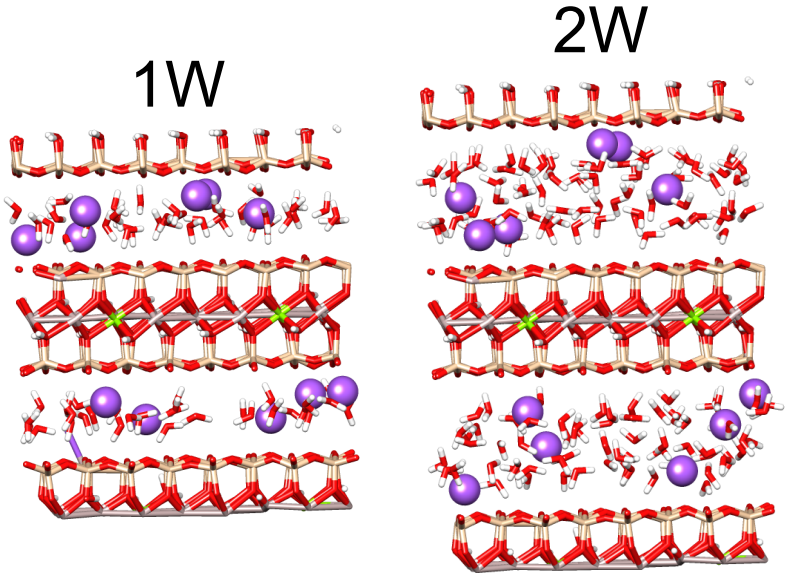


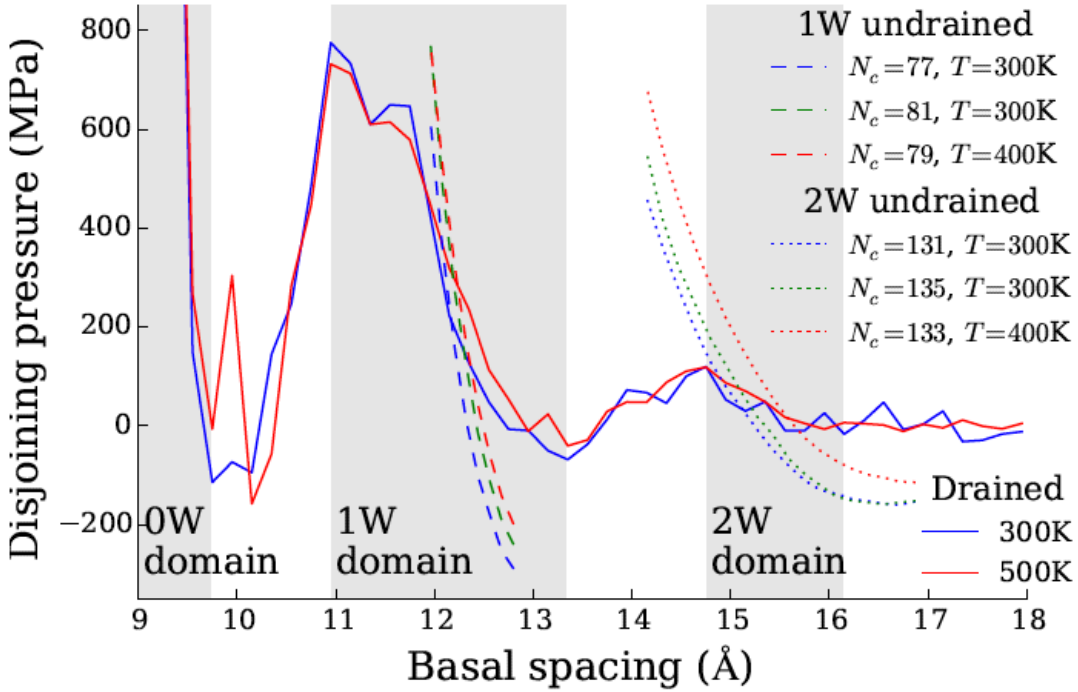
→ Need to account for the thermodynamics of the confined fluid in the poromechanics

Confined behavior by molecular simulation

- Drained ⇒ Grand Canonical Monte Carlo (long)
- Undrained ⇒ Molecular Dynamics (fast)

Saturated Na-Mnt





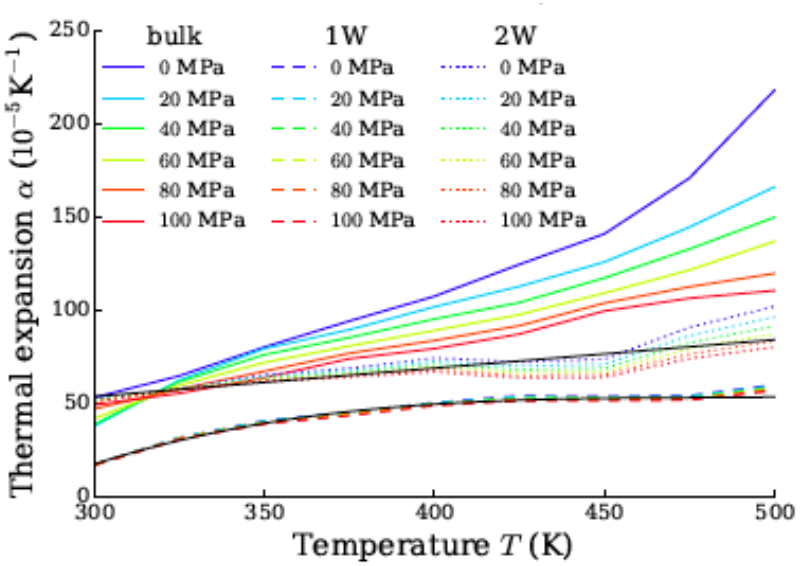
Confined behavior by molecular simulation

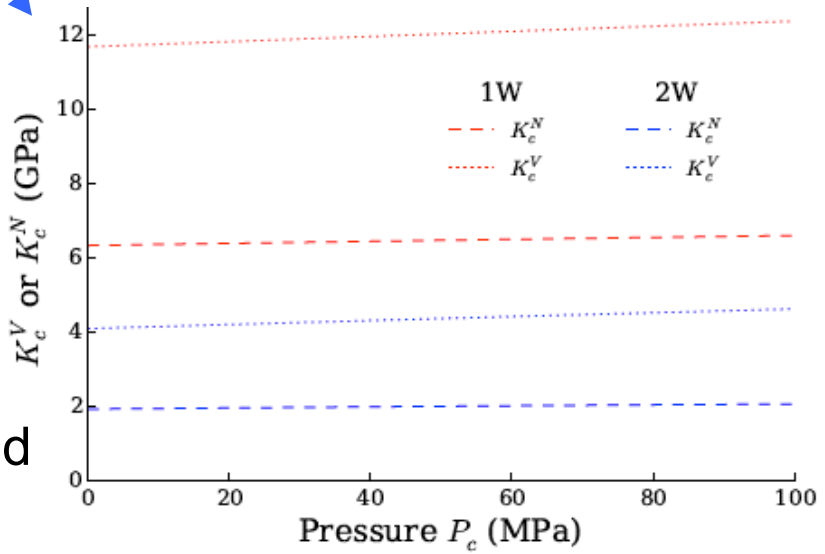
- Observation :
  - Thermal expansion lower than for bulk water
  - Strong difference between undrained volume and number rigidity ($K^V \sim 2\,K^N$)
  - Non negligible drained rigidity ($K^d \sim K^N$)
  - Some drained thermal expansion ($\alpha^s \ll \alpha^d \lesssim \alpha^u$)

⇒ Gibbs-Duhem not valid (confined behavior not extensive)

G-D ⇒ $K^V = K^N$ and $K^d = 0$ and $K^d \alpha^d = 0$

G-D ⇒ 3 thermo-mechanical moduli for a fluid





Thermodynamics of the confined fluid

- Usual fluid (Gibbs-Duhem valid): 3 moduli

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

- Confined fluid (Gibbs-Duhem not valid): 6 moduli

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

  - Volume and number rigidities differ: $K^V \neq K^N$
  - There is a non-zero drained rigidity: $K^d \neq 0$
  - There is a drained thermal-expansion: α^d

Usual thermo-poro-mechanics

- Elastic mechanical response of a porous solid submitted to
  - A change of deformation $d\varepsilon$
  - A change of pore pressure dP
  - A change of temperature dT

stress → $d\sigma = Kd\epsilon - bdP - K\alpha dT$

porosity → $d\phi = bd\epsilon + \frac{dP}{N} - \alpha_\phi dT$

entropy → $ds_s = K\alpha d\epsilon - \alpha_\phi dP + \frac{c}{T}dT$

K: bulk mod., b: Biot coef., N: Biot mod., α: thermal exp., c: heat capacity

Properties of the solid only

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

Note: case of an isotropic behavior limited to spherical response, can be generalized

Coussy, O. (2010) Mechanics and Physics of Porous Solids. Wiley & Sons

Usual thermo-poro-mechanics

- Elastic mechanical response of a porous solid submitted to
  - A change of deformation $d\varepsilon$
  - A change of pore pressure dP
  - A change of temperature dT

Maxwell relations for η_s

stress → $d\sigma = K d\epsilon - b dP - K\alpha dT$

porosity → $d\phi = b d\epsilon + \frac{dP}{N} - \alpha_\phi dT$

entropy → $ds_s = K\alpha d\epsilon - \alpha_\phi dP + \frac{c}{T} dT$

- Thermodynamics:
  - minimization of $\eta_s = f_s - \phi P$

Helmholtz free energy of the solid

Pairs of conjugated variables

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

Coussy, O. (2010) Mechanics and Physics of Porous Solids. Wiley & Sons

Consequence for thermo-poro-mechanics

- Pore (confined) pressure P_c ≠ outside (bulk) pressure P_b

  variable conjugated to the porosity — "what mechanical force is applied in the pores"

  control parameter — "what can be controlled by the experimentalist"

- Need to consider a new thermodynamic ensemble
  - Pore and outside fluid share the same chemical potential μ (osmotic equilibrium) → appropriate ensemble (ε, μ, T) instead of (ε, P_c, T)
  - Minimization of $\omega = f - \mu\phi\rho_c$

    f: Helmholtz free energy (solid + fluid)

    ρ_c: Fluid confined density

    μ: Fluid chemical potential
  - Energy balance

$dP_b - \rho_b d\mu - s_b dT = 0$ (Gibbs-Duhem)

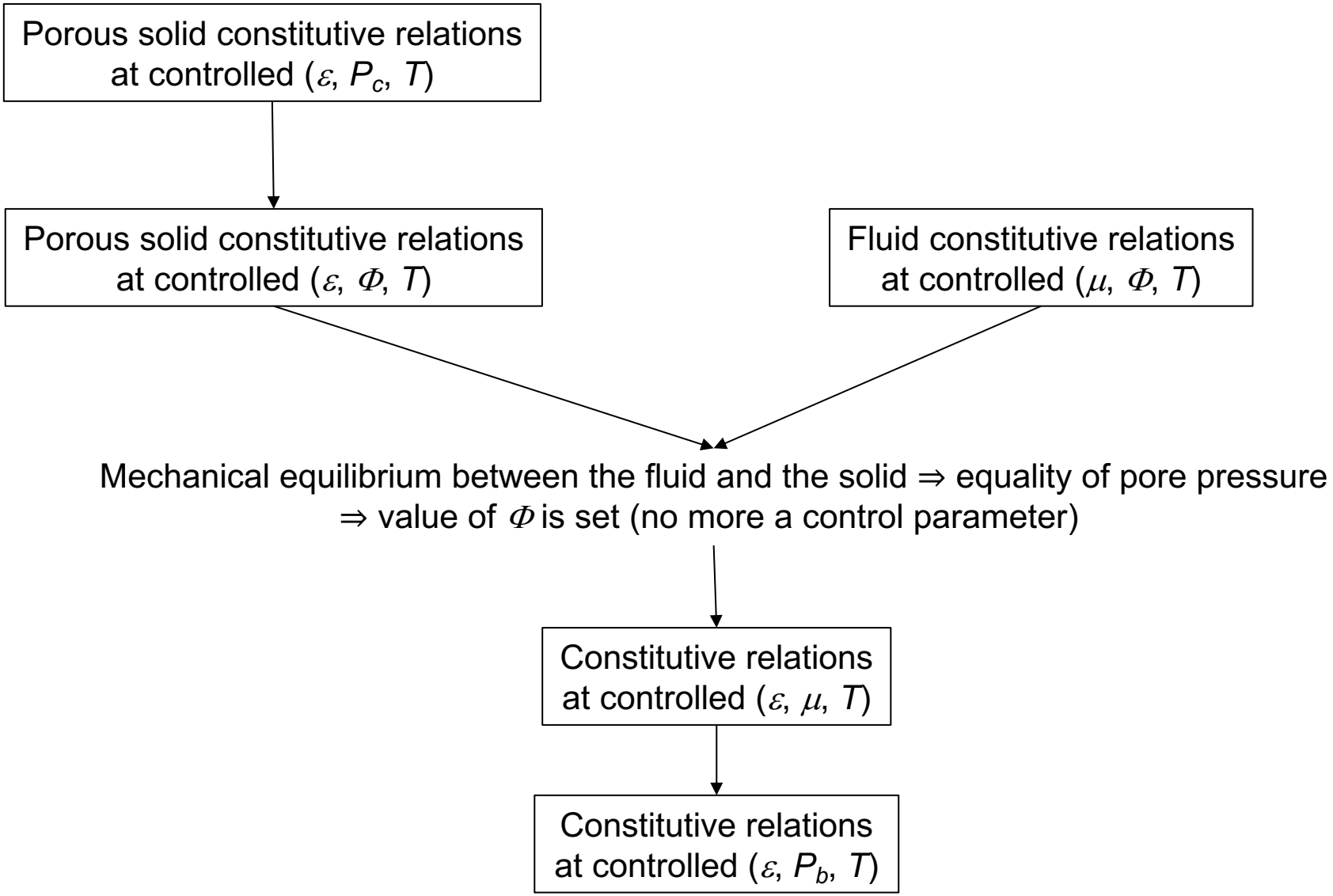
$$d\omega = \sigma d\epsilon - \phi\rho_c d\mu - s dT = \sigma d\epsilon - \phi^{eff} dP_b - s^{eff} dT$$

→ P_b conjugated to the effective porosity $\phi^{eff} = \dfrac{\phi\rho_c}{\rho_b}$

→ T conjugated to the effective entropy $s^{eff} = s - \phi^{eff} s_b$

The behavior at controlled bulk pressure (drained) is no more independent of the fluid

Constitutive relations



Constitutive relations

$$\begin{cases} d\sigma = K d\epsilon - b dP - K\alpha dT \\ d\phi = b d\epsilon + \frac{dP}{N} - \alpha_\phi dT \\ ds_s = K\alpha d\epsilon - \alpha_\phi dP + \frac{c}{T} dT \end{cases}$$ (ε, P_c, T)

K_c: bulk modulus
α_c: thermal exp.
c_c^v: heat cap. at cst. vol.

(ε, Φ, T)

$$\begin{cases} d\sigma = \left(K + Nb^2\right) d\epsilon - Nb d\phi - \left(K\alpha + Nb\alpha_\phi\right) dT \\ dP = -Nb d\epsilon + N d\phi + N\alpha_\phi dT \\ ds_s = \left(K\alpha + Nb\alpha_\phi\right) d\epsilon - N\alpha_\phi d\phi + \left(\frac{c}{T} - N\alpha_\phi^2\right) dT \end{cases}$$

Gibbs-Duhem

$$\begin{cases} dP_c = 0 \cdot d\phi + \rho_c d\mu + s_c dT \\ d\left(\phi\rho_c\right) = \rho_c d\phi + \frac{\phi\rho_c^2}{K_c} d\mu + \frac{\phi\rho_c}{K_c}\left(s_c - K_c\alpha_c\right) dT \\ d\left(\phi s_c\right) = s_c d\phi + \frac{\phi\rho_c}{K_c}\left(s_c - K_c\alpha_c\right) d\mu + \left(\frac{\phi c_c^v}{T} + \frac{\phi}{K_c}\left(s_c - K_c\alpha_c\right)^2\right) dT \end{cases}$$ (μ, Φ, T)

Mechanical equilibrium between the fluid and the solid ⇒ equality of pore pressure
⇒ value of Φ is set (no more a control parameter)

Constitutive relations at controlled (ε, μ, T)

Constitutive relations at controlled (ε, P_b, T)

Pb: Gibbs-Duhem not valid

$$\begin{cases} d\sigma = K d\epsilon - b dP - K\alpha dT \\ d\phi = b d\epsilon + \frac{dP}{N} - \alpha_\phi dT \\ ds_s = K\alpha d\epsilon - \alpha_\phi dP + \frac{c}{T} dT \end{cases} \quad (\varepsilon,\ P_c,\ T)$$

$$\downarrow \quad (\varepsilon,\ \Phi,\ T)$$

$$\begin{cases} d\sigma = \left(K + Nb^2\right) d\epsilon - N b d\phi - \left(K\alpha + Nb\alpha_\phi\right) dT \\ dP = -Nb d\epsilon + N d\phi + N\alpha_\phi dT \\ ds_s = \left(K\alpha + Nb\alpha_\phi\right) d\epsilon - N\alpha_\phi d\phi + \left(\frac{c}{T} - N\alpha_\phi^2\right) dT \end{cases}$$

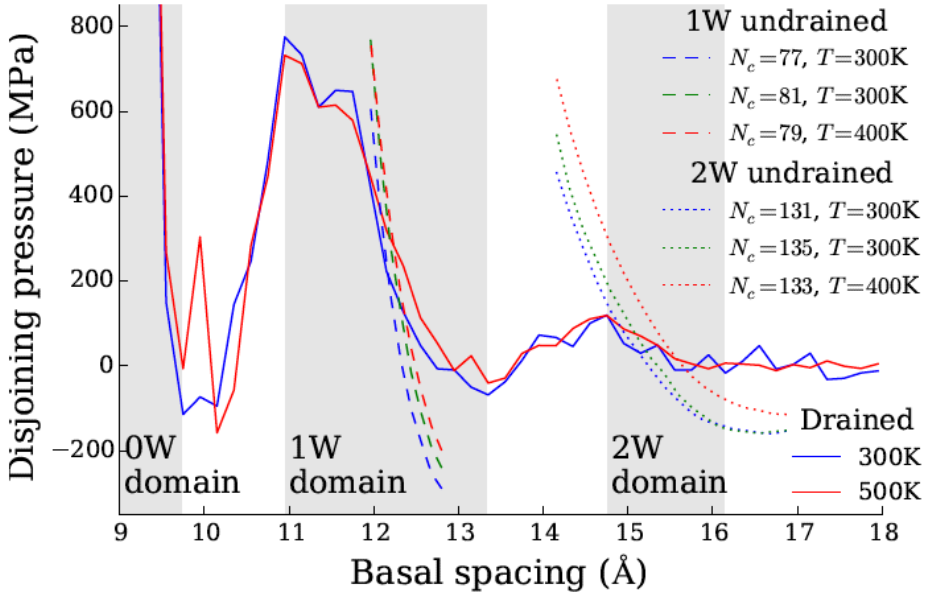
Not enough to fully describe the fluid behavior

K_c: bulk modulus
α_c: thermal exp.
c_c^v: heat cap. at cst. vol.

Gibbs-Duhem

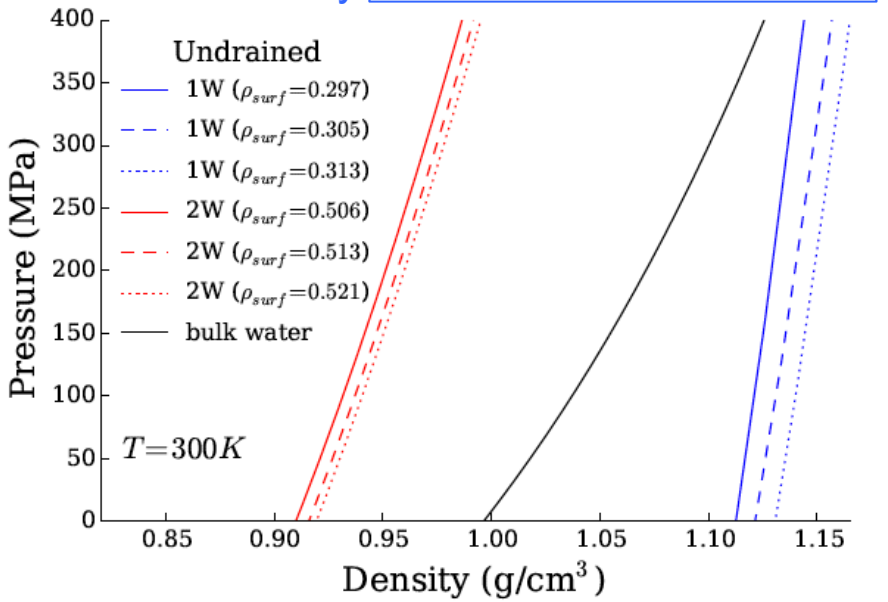
$$\begin{cases} dP_c = 0 \cdot d\phi + \rho_c d\mu + s_c dT \\ d\left(\phi\rho_c\right) = \rho_c d\phi + \frac{\phi\rho_c^2}{K_c} d\mu + \frac{\phi\rho_c}{K_c}\left(s_c - K_c\alpha_c\right) dT \\ d\left(\phi s_c\right) = s_c d\phi + \frac{\phi\rho_c}{K_c}\left(s_c - K_c\alpha_c\right) d\mu + \left(\frac{\phi c_c^v}{T} + \frac{\phi}{K_c}\left(s_c - K_c\alpha_c\right)^2\right) dT \end{cases} \quad (\mu,\ \Phi,\ T)$$

At cst. μ and T, pressure depends on Φ



Pressure is no more a function of density

$$-V_c \left.\frac{\partial P_c}{\partial V_c}\right|_T \neq N_c \left.\frac{\partial P_c}{\partial N_c}\right|_T$$



Pb: Gibbs-Duhem not valid

Gibbs-Duhem valid $\Leftrightarrow \delta = \gamma = 1$

$$\begin{cases} d\sigma = K d\epsilon - b dP - K\alpha dT \\ d\phi = b d\epsilon + \frac{dP}{N} - \alpha_\phi dT \\ ds_s = K\alpha d\epsilon - \alpha_\phi dP + \frac{c}{T} dT \end{cases} \quad (\varepsilon,\ P_c,\ T)$$

$$\downarrow \quad (\varepsilon,\ \Phi,\ T)$$

$$\begin{cases} d\sigma = \left(K + Nb^2\right) d\epsilon - Nb d\phi - \left(K\alpha + Nb\alpha_\phi\right) dT \\ dP = -Nb d\epsilon + N d\phi + N\alpha_\phi dT \\ ds_s = \left(K\alpha + Nb\alpha_\phi\right) d\epsilon - N\alpha_\phi d\phi + \left(\frac{c}{T} - N\alpha_\phi^2\right) dT \end{cases}$$

K_c: undr. rigidity w.r.t. nb
α_c^u: undr. th. exp.
c_c^v: heat cap. at cst. vol.

δ: undr. rigidity w.r.t. vol. / K_c
α_c^d: drained th. exp.
$1-\gamma$: drained rigidity / K_c

$$\begin{cases} dP_c = (\gamma - \delta)\frac{K_c}{\phi} d\phi + \gamma\rho_c d\mu + \gamma\rho_c \left(\frac{s_b}{\rho_b} + \frac{1-\gamma}{\gamma}\frac{K_c}{\rho_c}\alpha_c^d\right) dT \\ d\left(\phi\rho_c\right) = \gamma\rho_c d\phi + \gamma\frac{\phi\rho_c^2}{K_c} d\mu + \gamma\frac{\phi\rho_c^2}{K_c}\left(\frac{s_b}{\rho_b} - \frac{K_c}{\rho_c}\left(\frac{\delta}{\gamma}\alpha_c^u - \frac{1-\gamma}{\gamma}\alpha_c^d\right)\right) dT \\ d\left(\phi s_c\right) = \gamma\rho_c\left(\frac{s_b}{\rho_b} + \frac{1-\gamma}{\gamma}\frac{K_c}{\rho_c}\alpha_c^d\right) d\phi + \gamma\frac{\phi\rho_c^2}{K_c}\left(\frac{s_b}{\rho_b} - \frac{K_c}{\rho_c}\left(\frac{\delta}{\gamma}\alpha_c^u - \frac{1-\gamma}{\gamma}\alpha_c^d\right)\right) d\mu \\ \qquad + \left(\frac{\phi c_c^v}{T} + \gamma\frac{\phi\rho_c^2}{K_c}\left(\frac{s_b}{\rho_b} - \frac{K_c}{\rho_c}\left(\frac{\delta}{\gamma}\alpha_c^u - \frac{1-\gamma}{\gamma}\alpha_c^d\right)\right)^2\right) dT \end{cases} \quad (\mu,\ \Phi,\ T)$$

Mechanical equilibrium between the fluid and the solid ⇒ equality of pore pressure
⇒ value of Φ is set (no more a control parameter)

↓

Constitutive relations at controlled (ε, μ, T)

↓

Constitutive relations at controlled (ε, P_b, T)

Finally

$$\begin{cases} d\sigma = K d\epsilon - b dP - K\alpha dT \\ d\phi = b d\epsilon + \frac{dP}{N} - \alpha_\phi dT \\ ds_s = K\alpha d\epsilon - \alpha_\phi dP + \frac{c}{T} dT \end{cases} \quad (\varepsilon,\ P_c,\ T)$$

$$\begin{cases} d\sigma = \left(K + Nb^2\right) d\epsilon - Nb d\phi - \left(K\alpha + Nb\alpha_\phi\right) dT \\ dP = -Nb d\epsilon + N d\phi + N\alpha_\phi dT \\ ds_s = \left(K\alpha + Nb\alpha_\phi\right) d\epsilon - N\alpha_\phi d\phi + \left(\frac{c}{T} - N\alpha_\phi^2\right) dT \end{cases} \quad (\varepsilon,\ \Phi,\ T)$$

$$\begin{cases} dP_c = (\gamma - \delta)\frac{K_c}{\phi} d\phi + \gamma\rho_c d\mu + \gamma\rho_c \left(\frac{s_b}{\rho_b} + \frac{1-\gamma}{\gamma}\frac{K_c}{\rho_c}\alpha_c^d\right) dT \\ d\left(\phi\rho_c\right) = \gamma\rho_c d\phi + \gamma\frac{\phi\rho_c^2}{K_c} d\mu + \gamma\frac{\phi\rho_c^2}{K_c}\left(\frac{s_b}{\rho_b} - \frac{K_c}{\rho_c}\left(\frac{\delta}{\gamma}\alpha_c^u - \frac{1-\gamma}{\gamma}\alpha_c^d\right)\right) dT \\ d\left(\phi s_c\right) = \gamma\rho_c \left(\frac{s_b}{\rho_b} + \frac{1-\gamma}{\gamma}\frac{K_c}{\rho_c}\alpha_c^d\right) d\phi + \gamma\frac{\phi\rho_c^2}{K_c}\left(\frac{s_b}{\rho_b} - \frac{K_c}{\rho_c}\left(\frac{\delta}{\gamma}\alpha_c^u - \frac{1-\gamma}{\gamma}\alpha_c^d\right)\right) d\mu \\ \qquad + \left(\frac{\phi c_c^v}{T} + \gamma\frac{\phi\rho_c^2}{K_c}\left(\frac{s_b}{\rho_b} - \frac{K_c}{\rho_c}\left(\frac{\delta}{\gamma}\alpha_c^u - \frac{1-\gamma}{\gamma}\alpha_c^d\right)\right)^2\right) dT \end{cases} \quad (\mu,\ \Phi,\ T)$$

Mechanical equilibrium between the fluid and the solid ⇒ equality of pore pressure
⇒ value of Φ is set (no more a control parameter)

Usual structure satisfying Maxwell relations

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

- $K^{eff} = K + M^d b^2$ is the effective bulk modulus,
- $b^{eff} = \frac{\beta b \delta \rho_c}{\rho_b}$ is the effective Biot coefficient,

etc.

Brochard, L., & Honório, T. (2020). International Journal of Engineering Science, 152, 103296.

Comments

- Fluid properties are involved in all effective moduli (usual poromeca: moduli depend on solid only)

- One recovers usual poro-mechanics by considering $\delta = \gamma = 1$ (Gibbs-Duhem valid) and $\rho_c = \rho_b$

- Has been adapted to:
  - Undrained behavior
  - Double porosity media (micro- and macro-pores)

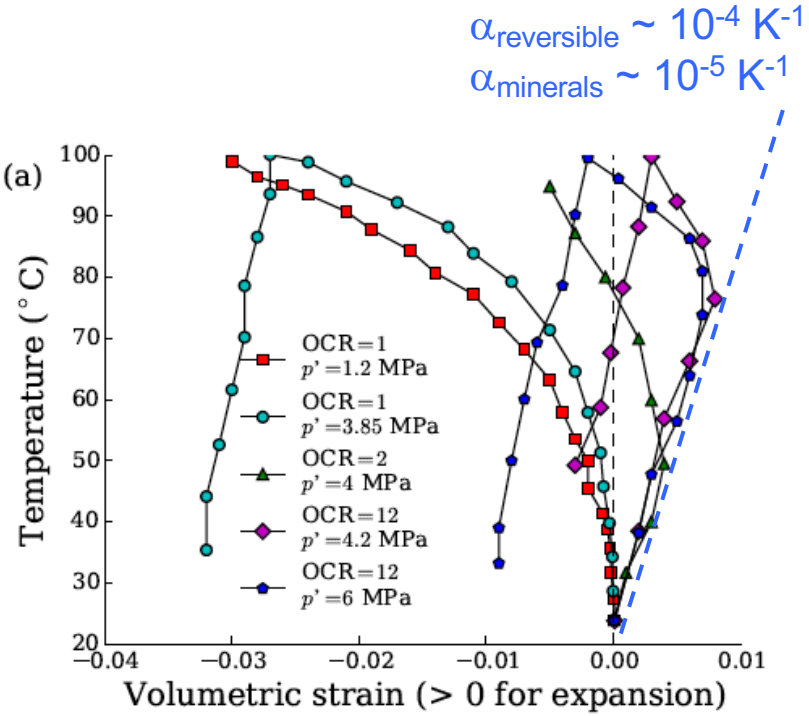
- <u>Main difficulty:</u> estimate confined fluid properties
  - Molecular simulation
  - Inverse analysis of well chosen experiments
  - Direct measurement (challenging)

Applications

- Drained thermal expansion

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

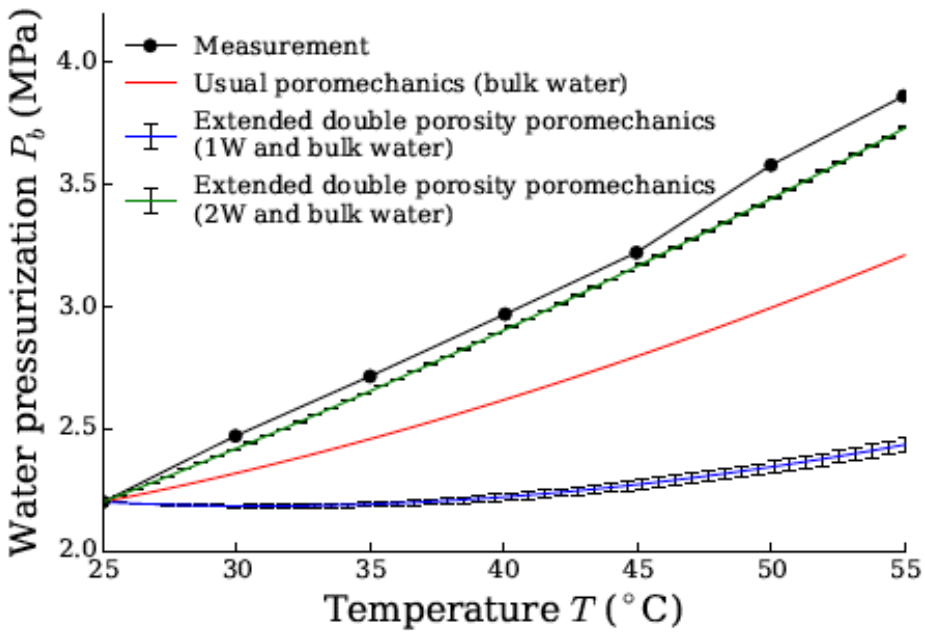
- Only without G-D can explain the large magnitude for clays
  - Th. exp. ~ 10^{-4} K^{-1}
  - Steel / concrete / minerals ~ 10^{-5} K^{-1}
  - Liq. H_2O (300K) = 2.10^{-4} K^{-1}



Source : experimental data from
Sultan (2002) Engineering Geology, 64(2-3), 135–145

Applications

- Fluid pressurization during undrained heating
  - Molecular simulation to estimate confined fluid properties
  - Double porosity approach proves essential (excess pressurization mostly due to fluid flow from micro- to macro-pores)



Property	1W water	2W water
K_c (GPa)	$7.1 - 0.012 \cdot (T - 300\text{K})$	$1.95 - 0.0035 \cdot (T - 300\text{K})$
δ	1.86	2.17
γ	0.16	-0.30
α_c^u (10^{-5}K^{-1})	$6.1863 \cdot 10^{-6} \cdot T^3 - 0.0088373 \cdot T^2 + 4.2189 \cdot T - 619.60$	$0.15231 \cdot T + 8.3333$
α_c^d (10^{-5}K^{-1})	36	15
ρ_c/ρ_b	1	1

Conclusions

- Revisit the poromechanics of clays to capture the effect of bound water
- Successfully reproduce THM anomalies
- Main messages
  - Confinement = more thermo-mechanical properties
  - Confined properties: to explore
  - Integration to poromechanics non-trivial
  - Fluid transfers between free and bound water are essential

Many thanks to

Tulio HONÓRIO
(former postodc, now LMPS & CEA)

Funding from:
- ANR – project TEAM2ClayDessicc (ANR-14-CE05-0023-01)
- CNRS NEEDS/MIPOR initiative project ARPENTONS

For more details:

Honório et al. (2017) Langmuir, 33(44), 12766-12776.

Brochard & Honório (2020) International Journal of Engineering Science, 152, 103296.

Brochard (2021) The Journal of Physical Chemistry C, 125(28), 15527-15543.

Brochard & Honório (2021) Acta Geotechnica, 16(9), 2713-2727.