Role of water adsorption in the thermo-mechanical behavior of clays

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Workshop “Clays: New Perspectives, Challenges & Opportunities”
1st anomaly: undrained heating experiment

- Excessive water pressurization

\[ \left. \frac{\partial P_b}{\partial T} \right|_{\sigma, \phi, \rho_b} = \frac{K M \phi}{K_u} (\alpha_b - \alpha_s) \]

**Interpretation:**
confined water thermal expansion higher than bulk water th. exp.

2\textsuperscript{nd} anomaly: drained heating experiment

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

\[ \alpha_{\text{irreversible}} \approx -10^{-3} \text{ K}^{-1} \]

\[ \alpha_{\text{reversible}} \approx 10^{-4} \text{ K}^{-1} \]

\[ \alpha_{\text{minerals}} \approx 10^{-5} \text{ K}^{-1} \]

Interpretation:
- Drainage of confined water

Objective: poromechanics capturing confinement

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

Clay matrix and inclusions (10 – 100 µm)

Stacks of layers (0.1 – 1 µm)

Clay layers (~ 10 nm)

Bulk water
= free water
= normal water

Confined water
= bound water
= adsorbed water

Confined water = normal water
Usual interpretations are non-obvious

- In adsorption community: confined th. exp. usually lower (e.g. Lennard-Jones in a slit pore)

\[
U_{ff} = 4\varepsilon \left( \left( \frac{\sigma}{r_{ff}} \right)^{12} - \left( \frac{\sigma}{r_{ff}} \right)^{6} \right)
\]

\[
U_{fs} = \varepsilon \left( \frac{2}{15} \left( \frac{\sigma}{r_{fs}} \right)^{9} - \left( \frac{\sigma}{r_{fs}} \right)^{3} \right)
\]

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<thead>
<tr>
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<th>0.02</th>
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<tbody>
<tr>
<td>bulk</td>
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- In adsorption community: confined th. exp. usually lower (e.g. Lennard-Jones in a slit pore)
- But water is not any liquid
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- In adsorption community: confined th. exp. usually lower (e.g. Lennard-Jones in a slit pore)
- But water is not any liquid
- Thermal expansion is not the only fluid property involved:

\[
\frac{\partial P_b}{\partial T}_{\sigma,\phi \rho_b} = \frac{KM\phi}{K_u} (\alpha_b - \alpha_s)
\]

- Undrained bulk modulus \( K_u = K + Mb^2 \)
- Undrained Biot modulus \( M = \frac{1}{N} + \frac{\phi}{K_b} \)
- Confined rigidity usually > bulk rigidity
Usual interpretations are non-obvious

- In adsorption community: confined th. exp. usually lower (e.g. Lennard-Jones in a slit pore)
- But water is not any liquid
- Thermal expansion is not the only fluid property involved
- Confined water is not undrained
  - Confined water is in osmotic equilibrium with free water
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 $P_b = \text{Cst}$

→ 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)
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 ($\alpha^s \ll \alpha^d \ll \alpha^u$)

$\Rightarrow$ Gibbs-Duhem not valid (confined behavior not extensive)

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

G-D $\Rightarrow$ 3 thermo-mechanical moduli for a fluid
Thermodynamics of the confined fluid

- Usual fluid (Gibbs-Duhem valid): 3 moduli
  \[
  \begin{aligned}
  dP_b &= -\frac{K_b}{V_b} dV_b + \frac{K_b}{N_b} dN_b + K_b \alpha_b dT \\
  d\mu &= -\frac{K_b}{N_b} dV_b + \frac{K_b V_b}{N_b^2} dN_b - \left(\frac{S_b}{N_b} - K_b \frac{V_b}{N_b} \alpha_b\right) dT \\
  dS_b &= K_b \alpha_b dV_b + \left(\frac{S_b}{N_b} - K_b \frac{V_b}{N_b} \alpha_b\right) dN_b + V_b \frac{c_v^b}{T} dT
  \end{aligned}
  \]

- Confined fluid (Gibbs-Duhem not valid): 6 moduli
  \[
  \begin{aligned}
  dP_c &= -\frac{K_c^V}{V_c} dV_c + \frac{K_c^N}{N_c} dN_c + K_c^V \alpha_c^u dT \\
  d\mu &= -\frac{K_c^N}{N_c} dV_c + \left(\frac{K_c^N}{K_c^N - K_c^d}\right) \frac{V_c}{N_c^2} dN_c - \left(\frac{S_b}{N_b} + \frac{K_c^N}{K_c^N - K_c^d} \frac{V_c}{N_c} \left(K_c^d \alpha_c^d - K_c^V \alpha_c^u\right)\right) dT \\
  dS_c &= K_c^V \alpha_c^u dV_c + \left(\frac{S_b}{N_b} + \frac{K_c^N}{K_c^N - K_c^d} \frac{V_c}{N_c} \left(K_c^d \alpha_c^d - K_c^V \alpha_c^u\right)\right) dN_c + \frac{V_c c_v^c}{T} dT
  \end{aligned}
  \]

- 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: $\alpha^d$
Revisited poromechanics

- Usual poromechanics
  - Control of the fluid pressure $P_b$

\[
\eta_s = f_s - \phi P
\]

\[
d\eta_s = \sigma : d\varepsilon - \phi dP - s_s dT
\]

\[
\begin{align*}
d\sigma &= K d\varepsilon - b dP - K \alpha dT \\
d\phi &= b d\varepsilon + \frac{dP}{N} - \alpha \phi dT \\
ds_s &= K \alpha d\varepsilon - \alpha \phi dP + \frac{\phi}{T} dT
\end{align*}
\]

- Revisited poromechanics
  - Control of the fluid chemical potential $\mu$ and temperature $T$

\[
\omega = f - \mu \phi \rho_c
\]

\[
d\omega = \sigma d\varepsilon - \phi \rho_c d\mu - s dT
\]

\[
\begin{align*}
d\sigma &= K_{\text{eff}} d\varepsilon - \beta b \delta \rho_c d\mu - (K_{\text{eff}} \alpha_{\text{eff}}^2 + b_{\text{eff}} s_b) dT \\
d(\phi \rho_c) &= \beta b \delta \rho_c d\varepsilon + \frac{\rho_b^2}{M^2} d\mu - \rho_b \alpha_{\mu}^{\text{eff}} dT \\
ds &= (K_{\text{eff}} \alpha_{\text{eff}}^2 + b_{\text{eff}} s_b) d\varepsilon - \rho_b \alpha_{\mu}^{\text{eff}} d\mu + \left( \frac{c_{\mu}^{\text{eff}}}{T} + M_{\text{eff}} \left( \alpha_{\mu}^{\text{eff}} \right)^2 \right) dT
\end{align*}
\]

\[
K_{\text{eff}} = K + M^d b^2
\]

\[
\frac{1}{M^d} = \frac{1}{N} + \frac{1}{\delta - \gamma} \frac{\phi}{K_C}
\]

\cdots
Thermal pressurization (undrained heating)

- Thermal pressurization coefficient

Usual poromech. \[ \frac{\partial P_b}{\partial T}_{\sigma, \phi \rho_b} = \frac{K_M \phi}{K_u} (\alpha_b - \alpha_s) \]

New poromech. \[ \frac{\partial P_b}{\partial T}_{\sigma, (\phi \rho)_{tot}} = \frac{\tilde{K}^{eff} \tilde{M}^{eff}}{\tilde{K}^{eff}_u} \left( \phi_b (\alpha_b - \alpha) + \left( \tilde{\beta} \frac{\delta \rho_c}{\rho_b} - \frac{\tilde{b}^{eff} \tilde{M}^d}{\tilde{K}^{eff}} b_c \right) \phi_c (\alpha^u_c - \alpha) \right. \]
\[ \left. + \left( \left( 1 - \tilde{\beta} \right) \frac{\delta \rho_c}{\rho_b} + \frac{\tilde{b}^{eff} \tilde{M}^d}{\tilde{K}^{eff}} b_c \right) \phi_c \left( \alpha^u_c - \frac{1 - \gamma}{\delta - \gamma} \alpha^d_c \right) \right) \] (21)

- Salient features:
  - No Gibbs-Duhem
  - Thermo-mechanical couplings
  - Double porosity
Confrontation with experiment

- New poromechanics captures experiment if the confined water is 2W water
- The main origin of the anomalous pressurization is the less intuitive contribution (difference between thermal expansion at constant $P_b$ and at constant $P_c$)
Drained heating

- **Reversible expansion**: also captured by new poromechanics
- **Irreversible contraction**: model based on transition between hydration states inspired by shape memory alloys (qualitative)

Conclusions

- Revisit the poromechanics of clays starting from confined water
- Successfully reproduce THM anomalies
- Main messages
  - Confinement = more thermo-mechanical properties
  - Fluid transfers between free and bound water are essential
- Perspectives
  - Explore confined fluid properties
  - Extend to irreversible contraction
Thank you for your attention

T. Honorio
(postdoc)

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