Poroelasticity theory of chemically active clay shales*

Bunyod Imomnazarov, Kholmatzhon Imomnazarov

Abstract. The deformation tensor ε in a porous medium is a function of the stress tensor σ and the pore pressure p. Additional osmotic effects are present in some rocks, such as shales. It is shown that such effects, in turn, modify the thermodynamics of the system, namely, in terms of the internal energy of the additional term due to the chemical potential μ^r of all the chemical components in the pore fluid. Because of this, an additional term due to the chemical potentials appears in the strain-stress relations.

Keywords: porous medium, saturated fluid, elastic parameters, stress tensor, partial density, Darcy law, chemical potential.

Clays are one of the most common types of rocks that make up to 11 % of the entire volume of the Earth's crust. They are often associated with constructing the foundations of buildings and various engineering structures. They are everywhere used as raw materials for the production of ceramics, bricks, cement, as well as fillers in manufacturing rubber, paper, drilling fluids, etc. Clays have a high adsorption capacity, and are successfully used for cleaning oils, paints, wines, bleaching of fabrics, and, also, as natural ecological barriers for the technogenic pollutions control [1].

1. Thermodynamics of a two-phase medium with surfacant

Let us consider a two-phase medium with thermodynamic equilibrium in the volume V, which is a fluid with droplets in it, and these droplets may be, for example, oil. Let us denote the water mass within the indicated volume as M_1, the oil mass as M_2, and the surfactant mass as M_c. The first principle of thermodynamics mentioned below introduces a version of the hydrodynamic system analyzed here [2]:

$$d\tilde{E}_0 = T\, d\tilde{S} - p\, dV + \mu_1\, dM_1 + \mu_2\, dM_2 + \mu_c\, dM_c + \tilde{\sigma}\, d\tilde{\Sigma}. \qquad (1)$$

Here $\tilde{E}_0$, $\tilde{S}$ are the internal energy and the entropy of the system within the volume V; T is the temperature; p is the pressure; $\tilde{\sigma}$ is the surface tension at the interface between water and oil; $\tilde{\Sigma} = \zeta J$ is the total surface area of

the interface between water and oil droplets; J is the number of droplets in the volume; μ_1, μ_2, μ_c are the chemical potentials of components 1, 2, and surfactant. The pressure drop in "fluidic subsystems" may be neglected in further considerations. Equation (1) introduces the chemical potentials [3]. For the hydrodynamic description, we need to introduce the physical densities:

$$(\tilde{E}_0, \tilde{S}, M_1, M_2, M_c, \tilde{\Sigma}) = (E_0, S, \rho_1, \rho_2, \rho_c, \zeta\, J)\, V. \tag{2}$$

Substituting the relationships from (2) into (1), we arrive at the first principle of thermodynamics for a unit volume of the medium:

$$dE_0 = T\, dS - p\, dV + \mu_1\, d\rho_1 + \mu_2\, d\rho_2 + \mu_c\, d\rho_c + \zeta\tilde{\sigma}\, dJ. \tag{3}$$

The pressure can be found via the thermodynamic formula [4]

$$p = -E_0 + TS + \mu_1\rho_1 + \mu_2\rho_2 + \mu_c\rho_c + \zeta\tilde{\sigma}J.$$

Let us introduce the density of a medium containing water, oil, and surfactant:

$$\rho = \rho_1 + \rho_2 + \rho_c.$$

In terms of the new variables, formula (3) takes the following form:

$$dE_0 = T\, dS + \mu_1\, d\rho + (\mu_2 - \mu_1)\, d\rho_2 + (\mu_c - \mu_1)\, d\rho_c + \zeta\tilde{\sigma}\, dJ.$$

Because the relationship $\rho_2 = M/V = m\, N/V = m\, J$ holds, we arrive at the local form of the first principle of thermodynamics of the four-parameter thermodynamic system [5]

$$\begin{aligned}
dE_0 &= T\, dS + \mu_1\, d\rho + \zeta\bar{\sigma}\, dJ + (\mu_c - \mu_1)\rho_c \\
&= T\, dS + \mu_1\, d\rho + \frac{\zeta\bar{\sigma}}{m}\, d\rho_2 + (\mu_c - \mu_1)\rho_c \\
\bar{\sigma} &= \tilde{\sigma} + \frac{m}{\zeta}(\mu_2 - \mu_1), \\
p &= -E_0 + TS + \mu_1\rho + (\mu_c - \mu_1)\rho_c + \zeta\bar{\sigma}J, \\
dp &= S\, dT + \rho\, d\mu_1 + \rho_c\, d(\mu_c - \mu_1) + \zeta J\, d\bar{\sigma}.
\end{aligned} \tag{4}$$

Here m is the mass of a droplet, $\mu_2 \neq \mu_1$.

Formula (4) describes a local thermodynamic equilibrium. For a relative mutual motion of two components, we need to generalize the theory [6] for the case without local equilibrium. The velocity difference $\boldsymbol{w} = \boldsymbol{u} - \boldsymbol{v}$ of the water–oil continuum may be considered to be a relaxing degree of freedom [7]:

$$dE_0 = T\,dS + \mu_1\,d\rho + \zeta\bar{\sigma}\,dJ + (\mu_c - \mu_1)\,d\rho_c + (\boldsymbol{u} - \boldsymbol{v})\,d\boldsymbol{j}_0$$

$$= T\,dS + \mu_1\,d\rho + \frac{\zeta\bar{\sigma}}{m}\,d\rho_2 + (\mu_c - \mu_1)\,d\rho_c + (\boldsymbol{u} - \boldsymbol{v})\,d\boldsymbol{j}_0,$$

$$p = -E_0 + TS + \mu_1\rho + (\mu_c - \mu_1)\rho_c + \zeta\bar{\sigma}J + (\boldsymbol{u} - \boldsymbol{v})\boldsymbol{j}_0,$$

$$dp = S\,dT + \rho\,d\mu_1 + \rho_c\,d(\mu_c - \mu_1) + \zeta J\,d\bar{\sigma} + \boldsymbol{j}_0\,d(\boldsymbol{u} - \boldsymbol{v}).$$

Here, $\boldsymbol{j}_0$ is the density of a relative momentum of the two components; $\boldsymbol{u}$ is the velocity of the droplet continuum; v is the velocity of the water continuum. The kinetic term for the two-velocity medium was introduced as recommended by Landau [4].

2. Deformation-stress relations with allowance for chemical potentials

Let f be the Helmholtz free energy of the porous system (that is, the skeleton of the pore fluid) of the temperature T and of the entropy per unit volume S of the porous body. We have

$$df = \sigma_{ij}\,d\varepsilon_{ij} + \sum_{r=1}^{R} \mu^r dm^r - S\,dT.$$

Here the solvent (usually water) and $(R-1)$ of other species are in the pore fluid. The mass m^r of each species per unit volume of a porous material is measured in moles.

The chemical potentials of the components in the solution can be written down in the form [8]

$$\mu^r = \mu_0^r + RT\ln x^r\gamma^r = \mu_0^r + RT\ln a^r.$$

Here μ_0^r is the chemical potential of the form r in the equilibrium state, x^r is the partial molar fraction of the species r, Γ^r is the activity coefficient, $a^r = x^r\gamma^r$ is the activity of the rth kind, and R is the gas constant. In an ideal solution, $\gamma^r = 1$. The chemical potential μ_0^r is the function of pressure and satisfies the relation

$$\frac{\partial\mu_0^r}{\partial p} = v^r = \frac{1}{\rho^r},$$

where v^r is the volume of one mole of the substance.

Further, we neglect the effect of temperature. Usually, in laboratory conditions, this is done. We define the Helmholtz free energy f_0 associated with a solid particle in the form

$$df_0 = d(f - \mu^r m^r) = \sigma_{ij}\,d\varepsilon_{ij} - \sum_{r=1}^{R} m^r d\mu^r.$$

This is because df_0 is a complete differential. Taking ε_{ij} and μ^r as independent state variables, we obtain

$$\frac{\partial \sigma_{ij}}{\partial \mu^r} = -\frac{\partial m^r}{\partial \varepsilon_{ij}}, \tag{5}$$

$$\frac{\partial m^r}{\partial \mu^s} = \frac{\partial m^s}{\partial \mu^r}. \tag{6}$$

Thus, in these variables the strain-stress relationship has the form

$$d\sigma_{ij} = C_{ijkl}\, d\varepsilon_{kl} - \sum_r D_{ij}^r\, d\mu^r, \tag{7}$$

$$dm^r = D_{ij}^r\, d\varepsilon_{ij} + \sum_s A^{rs} d\mu^s, \tag{8}$$

where we used (5) to determine the cross-ratio D_{ij}^r in (7) and (8), and where by virtue of (6) $A^{rs} = A^{sr}$. In addition, we can consider the Gibbs free energy

$$d\left(f - \sum_r \mu^r m^r - \sigma_{ij}\varepsilon_{ij}\right) = \varepsilon_{ij}\, d\sigma_{ij} - \sum_r m^r d\mu^r.$$

Again, by virtue of the total differential, and taking σ_{ij} and μ^r as variables of state, we obtain

$$\frac{\partial \varepsilon_{ij}}{\partial \mu^r} = \frac{\partial m^r}{\partial \sigma_{ij}}, \tag{9}$$

and, as before, relation (6) holds. Consequently,

$$d\varepsilon_{ij} = S_{ijkl}\, d\sigma_{kl} + \sum_r Q_{ij}^r\, d\mu^r, \tag{10}$$

$$dm^r = Q_{ij}^r\, d\sigma_{ij} + \sum_s B^{rs} d\mu^s, \tag{11}$$

where we used (9) to determine the cross-ratio Q_{ij}^r in (10) and (11), and where by virtue of (7) $B^{rs} = B^{sr}$.

Next, we use the stress σ_{ij} and the chemical potentials μ^r as independent variables of state, and we use relations (10) and (11). The coefficients S_{ijkl}, Q_{ij}^r, and B^{sr} appearing in these relations are determined from the experiments. The experiments on compaction of clay in contact with a large reservoir were performed in [9, 10]. In each experiment, the composition of the formation fluid was maintained to be constant, and the applied voltage varied: the results give information on the coefficients S_{ijkl}. The chemical composition of the fluid of the oil pool varied within the same experiment,

either by changing the solution CaCl$_2$ by the solution NaCl, or by changing the salt concentration. Observation of the degree of swelling of clays as a function of the salt concentration can also be performed at a microscopic level, using X-ray diffraction to measure the distance between the clay particles (see, for example, [11, 12]). Thus, such information allows us to determine the cross coefficients Q_{ij}^r.

3. The one-component pore fluid

In a single-component pore fluid, $a^r = x^r = \gamma^r = 1$, and, therefore, according to formula (1), $\mu^1 = dp/d\rho^1$. The response of the shale will depend only on the pore pressure p of the liquid in the reservoir and the applied voltage σ_{kl}. If the system is isotropic, relations (10) and (11) are simplified and take the form

$$d\varepsilon_{ij} = S_1\, d\sigma_{ij} + S_2\delta_{ij}\, d\sigma_{kk} + \delta_{ij} \sum_r Q^r d\mu^r, \tag{12}$$

$$dm^r = Q^r d\sigma_{kk} + \sum_s B^{rs} d\mu^s, \tag{13}$$

and it is evident that for the modeling four material coefficients are required. In an isotropic porous medium, relations (12) and (13) can be written in the form [13]

$$2\mu\varepsilon_{ij} = \sigma_{ij} - \frac{\nu}{\nu+1}\, \sigma_{kk}\delta_{ij} + \frac{3(\nu_u - \nu)}{B(\nu+1)(\nu_u+1)}\, \sigma_{kk} p\, \delta_{ij},$$

$$m - m_0 = \frac{3\rho_0(\nu_u - \nu)}{2\mu B(\nu+1)(\nu_u+1)}\left(\sigma_{kk} + \frac{3}{B}\, p\right).$$

Here we have chosen the four material coefficients: the shear modulus μ, the saturated and unsaturated Poisson coefficients ν and ν_u, and the Skempton parameter B, which connects the unsaturated response of the pore pressure and the applied stress.

4. Equations of motion

If deviations from the thermodynamic equilibrium are inessential, then the mass flow of the $\boldsymbol{q}^r$ of rth kind can be represented in the form

$$q_i^r = -\sum_s L_{ij}^{rs} \nabla_j \mu^s,$$

where according to the Onsager principle $L_{ij}^{rs} = L_{ij}^{sr}$. Since in this study we consider single-component pore fluids, the saturable porous media are taken to be isotropic, and for such media in the hydraulic case the Darcy law holds [5, 14]:

$$\boldsymbol{q}^1 = -\frac{1}{\chi\rho\rho^1}\nabla p,$$

where ρ^1 is the partial density of the pore liquid (water), ρ is the total density of the continuum, χ is the interfacial friction coefficient. The law of conservation of mass for each species is valid

$$\frac{\partial m^r}{\partial t} + \operatorname{div} \boldsymbol{q}^r = 0,$$

and, hence,

$$\frac{\partial}{\partial t}\left(Q_{ij}^r d\sigma_{ij} + \sum_s B^{rs} d\mu^s\right) = \frac{\partial}{\partial x_i}\left(\sum_s L_{ij}^{rs} \nabla_j \mu^s\right).$$

The electroneutrality requires that there should be no build-up in a charge at any point. If z^r is the valency of the rth type, then

$$\frac{\partial}{\partial x_i}\left(\sum_r q_i^r z^r\right) = 0.$$

The streaming potentials will be created for preserving electrical neutrality. It is convenient to explicitly introduce the streaming potential Ψ, and to write the chemical potentials of the rth kind in the following way $\mu^r = \hat{\mu}^r + z^r F\Psi$, where $\hat{\mu}^r$ is the chemical potential (the rth kind) corresponding to the local concentration of ions, water, and clay. The ionic flows take the form

$$q_i^r = -\sum_s L_{ij}^{rs} \frac{\partial}{\partial x_j}(\hat{\mu}^s + z^s F\Psi),$$

and the streaming potential Ψ is the solution to the Poisson equation of the following form

$$\sum_r z^r \frac{\partial}{\partial x_i}\left(\sum_s L_{ij}^{rs} \frac{\partial}{\partial x_j}(\hat{\mu}^s + z^s F\Psi)\right) = 0$$

with zero Dirichlet boundary condition for the contact with a high conductivity of a fluid or a porous rock.

If flows are specified, then the conditions of non-flow and non-conducting boundaries are satisfied. If an ion is adsorbed on the walls of the pores, it will travel only slowly through the rocks, and the corresponding transfer coefficients L_{ij}^{rs} will be small. If the chemical effects are negligible (for example, if the porosity within the shale, due to the outflow is essential), then the convective currents will dominate with additional diffusion of ions with respect to the fluid volume.

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