Derivation of the equation for hydraulic pressure

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The aim is to relate Thomson equation, poromechanic equations for unsaturated media in order to obtain the value of the liquid pressure during freezing. This is the detailed version of the derivation made in *Mechanics and Physics of Porous Solids* by O. Coussy. To simplify the calculation, we will take the atmospheric pressure as the 0 pressure.

Let us start with the conservation of matter :

$$n = \frac{\phi_C}{\upsilon_C} + \frac{\phi_L}{\upsilon_L} \tag{1}$$

$$n = \frac{\phi_0 S_C + \varphi_C}{\upsilon_C} + \frac{\phi_0 S_L + \varphi_L}{\upsilon_L} \tag{2}$$

Using the definition of the Lagrangian definition with the pore space deformation.

$$n = \underbrace{\phi_0 S_C \left[\frac{1}{\upsilon_C} - \frac{1}{\upsilon_C^0}\right]}_{A} + \frac{\phi_0 S_C}{\upsilon_C^0} + \underbrace{\phi_0 S_L \left[\frac{1}{\upsilon_L} - \frac{1}{\upsilon_L^0}\right]}_{B} + \frac{\phi_0 S_L}{\upsilon_L^0} + \frac{\varphi_C}{\upsilon_C} + \frac{\varphi_L}{\upsilon_L} \tag{3}$$

$$n = \tag{4}$$

A (respectively B) corresponds to the change of the solid (resp. liquid) phase volume because of the change of molar volume of the solid (resp. liquid).

$$n = A + B + \underbrace{\phi_0 S_C \left[\frac{1}{\upsilon_C^0} - \frac{1}{\upsilon_L^0}\right]}_{C} + \frac{\phi_0 S_C}{\upsilon_L^0} + \frac{\phi_0 S_L}{\upsilon_L^0} + \frac{\varphi_C}{\upsilon_C} + \frac{\varphi_L}{\upsilon_L} \tag{5}$$

C corresponds to the variation of volume when transforming from the liquid to the solid phase.

$$n = A + B + C + \underbrace{\frac{\phi_0}{\upsilon_L^0}\left(\phi_C + \phi_L\right)}_{D} + \frac{\varphi_C}{\upsilon_C} + \frac{\varphi_L}{\upsilon_L} \tag{6}$$

we have $S_C + S_L = 1$, so $D = \frac{\phi_0}{\upsilon_L^0} = n_0$ i.e. the initial quantity of matter in the porosity considering that all is under liquid form.

$$n = n_0 + A + B + C + \varphi_C \left[\frac{1}{\upsilon_C^0} - \frac{1}{\upsilon_L^0}\right] + \varphi_L \left[\frac{1}{\upsilon_L^0} - \frac{1}{\upsilon_C^0}\right] + \frac{\varphi_C + \varphi_L}{\upsilon_L^0} \tag{7}$$

Considering small deformations and that the change of molar volume between liquid and solid form is also very small (9% for water), the terms $\varphi_C \left[\frac{1}{\upsilon_C^0} - \frac{1}{\upsilon_L^0}\right]$ and $\varphi_L \left[\frac{1}{\upsilon_L^0} - \frac{1}{\upsilon_C^0}\right]$ are second order terms and then can be neglected. As a result be obtain :

$$n = n_0 + \phi_0 S_C \left[\frac{1}{\upsilon_C} - \frac{1}{\upsilon_C^0}\right] + \phi_0 S_L \left[\frac{1}{\upsilon_L} - \frac{1}{\upsilon_L^0}\right] + \phi_0 S_C \left[\frac{1}{\upsilon_C^0} - \frac{1}{\upsilon_L^0}\right] + \frac{\varphi_C + \varphi_L}{\upsilon_L^0} \tag{8}$$

The state equation for condensed phases is $\frac{d\rho}{\rho} = \frac{p}{K} - \alpha\left(T - T_m\right) \Leftrightarrow \frac{1}{\upsilon} = \frac{1}{\upsilon_0}\left[1 + p/K - \alpha\left(T - T_m\right)\right]$. we then have :

$$A = \phi_0 S_C \left[\frac{1}{\upsilon_C} - \frac{1}{\upsilon_C^0}\right] \tag{9}$$

$$A = \frac{\phi_0 S_C}{\upsilon_C^0}\left[\frac{p_C}{K_C} - \alpha_C (T - T_m)\right] \tag{10}$$

$$B = \frac{\phi_0 S_L}{\upsilon_L^0}\left[\frac{p_L}{K_L} - \alpha_L (T - T_m)\right] \tag{11}$$

Then using the unsaturated poromechanics equations for the variation of porosity :

$$\frac{\varphi_C + \varphi_L}{\upsilon_L^0} = \frac{1}{\upsilon_L^0}\left[b_C\epsilon + b_L\epsilon + p_C\left(\frac{1}{N_C} + \frac{1}{N_{CL}}\right) + p_L\left(\frac{1}{N_L} + \frac{1}{N_{CL}}\right) - \left(\alpha_C + \alpha_L\right)\left(T - T_m\right)\right] \tag{12}$$

$$= \frac{1}{\upsilon_L^0}\left[b\epsilon + p_C\frac{b_C - \phi_0 S_C}{K_{sk}} + p_L\frac{b_L - \phi_0 S_L}{K_{sk}} - \left(\alpha_C + \alpha_L\right)\left(T - T_m\right)\right] \tag{13}$$

$$\tag{14}$$

with $\frac{1}{N_J} + \frac{1}{N_{IJ}} = \frac{b_J - \phi_0 S_J}{K_{sk}}$.

Using now the first equation of unsaturated poromechanics $\sigma = K\epsilon - bS_C p_C - bS_L p_L - \alpha_{sk}\left(T - T_m\right)$:

$$\frac{\varphi_C + \varphi_L}{\upsilon_L^0} = \frac{1}{\upsilon_L^0}\left[\frac{b\sigma}{K} + \frac{b^2}{K}\left(S_C p_C + S_L p_L\right) + \alpha_{sk} b (T - T_m) + \frac{b - \phi_0}{K_{sk}}\left(p_C S_C + p_L S_L\right) - \left(\alpha_C + \alpha_L\right)\left(T - T_m\right)\right] \tag{15}$$

Using now $\frac{1}{N} = \frac{b - \phi_0}{K_{sk}}$, we have :

$$\frac{\varphi_C + \varphi_L}{\upsilon_L^0} = \frac{1}{\upsilon_L^0}\left[\frac{b\sigma}{K} + \left(S_C p_C + S_L p_L\right)\left(\frac{b^2}{K} + \frac{1}{N}\right) - \left(\alpha_C + \alpha_L - b\alpha_{sk}\right)\left(T - T_m\right)\right] \tag{16}$$

Combining now the previous equation with the expressions of A and B, we obtain for the pressure terms :

$$\Delta n_2 = \frac{1}{\upsilon_L^0}\left[\frac{b\sigma}{K} + S_C p_C\left(\frac{\phi_0}{K_C}\frac{\upsilon_L^0}{\upsilon_C^0} + \frac{1}{N} + \frac{b^2}{K}\right) + S_L p_L\left(\frac{\phi_0}{K_L} + \frac{1}{N} + \frac{b^2}{K}\right)\right] \tag{17}$$

and for the temperature terms :

$$\Delta n_3 = \frac{1}{\upsilon_L^0}\left(-\alpha_C - \alpha_L + b\alpha_{sk} - \alpha_C\phi_0 S_C\frac{\upsilon_L^0}{\upsilon_C^0} - \alpha_L\phi_0 S_L\right)\left(T - T_m\right) \tag{18}$$

$$\Delta n_3 = \frac{\phi_0}{\upsilon_L^0}\left(\alpha_{sk} - S_C\alpha_C\frac{\upsilon_L^0}{\upsilon_C^0} - S_L\alpha_L\right)\left(T - T_m\right) \tag{19}$$

Finally, we obtain for the evolution of the mole quantity in the pores :

$$n - n_0 = \phi_0 S_C\left[\frac{1}{\upsilon_C^0} - \frac{1}{\upsilon_L^0}\right] + \Delta n_2 + \Delta n_3 \tag{20}$$

In order to continue, we need to make some approximations. First of all let us restrict ourselves to water. We then have $K_L = 2.2$GPa and $K_C = 8.8$GPa. Usually, the bulk modulus for a porous solid and the bulk modulus of the material composing the matrix are larger than 20GPa. Accordingly, we can neglect $\frac{1}{N} + \frac{b^2}{K}$ when compared to $\phi_0/K_{L,C}$

The order of magnitude of the thermal coefficient α_J is 10^{-5} K^{-1} and the melting entropy of water is $\Delta s_m = 1.2$MPa.K^{-1}. As a result, Δn_3 is negligible in the mole equation.

Finally, injecting Thomson equation $p_C - p_L + \left(1 - \frac{\upsilon_L^0}{\upsilon_C^0}\right) p_L = \Delta s_m \left(T - T_m\right)$ in Δn_2, we obtain :

$$n - n_0 \approx \frac{b\sigma}{K\upsilon_L^0} + \phi_0 \left(\frac{S_L}{K_L} + \frac{S_C}{K_C}\right) \frac{p_L}{\upsilon_L^0} - \phi_0 S_C \left[\frac{1}{\upsilon_L^0} - \frac{1}{\upsilon_C^0}\right] \tag{21}$$

The first term of this relation accounts for the mole change made possible by the change in pore volume due to external stress. This change in pore volum is podsitive for a tensile srtess, that is for $\sigma > 0$, and negative for a compressive stress, that is for $\sigma < 0$. [...] the second term accounts for the mole change made possible by the decrease in voume of the current in-pore phases cyased by their deformation. In contrast, the increase of volume due to the phase change opposes an increase of the mole density n, which is accounted for by the last term. (Coussy 2010).

If we consider now an undrained case (i.e. $n - n_0 = 0$) and a stress free experiment, we obtain finally :

$$p_L = S_C \left(1 - \frac{\upsilon_L^0}{\upsilon_C^0}\right) \frac{K_L K_C}{K_L S_L + K_C S_C} \tag{22}$$