Keynote

Lectures
Physical Mechanics of In-Pore Phase Transition

O. Coussy*

*Université Paris-Est,
Ecole des Ponts
Institut Navier
6-8 Av. Blaise Pascal - Cité Descartes
F 77455 Marne-la-Vallée Cedex 2
France
Olivier.Coussy@mail.enpc.fr

ABSTRACT: In this paper we show how the mechanics of confined phase transition within a deformable porous solid can be addressed in a unique framework, whatever the phase transition considered, either the liquid-gas transition involved in the drying of porous materials or the liquid-solid transition involved in their freezing. Indeed, owing to stability considerations a hydrostatic stress is shown to ultimately prevail within the solid crystal phase so that the latter behaves like a compressible elastic fluid as long as only in-pore phase transition is involved. The extension of saturated poroelasticity to unsaturated conditions allows us to work out appropriate constitutive equations to capture the deformation resulting from in-pore phase transition within an elastic porous solid, while the use of homogenization schemes provides estimates of the unsaturated poroelastic theses constitutive equations involve. The prediction of the drying shrinkage or that of the deformation due to cryosuction during freezing reveals the significant effect of the pore size distribution, since the intensity of both the deformation and the elastic energy that the solid matrix can store strongly depends upon the homogenization scheme.

KEY WORDS: poroelasticity, pore size distribution, homogenization, drying shrinkage, crystallization.
1. Introduction

The understanding of the mechanical behaviour of porous materials upon confined phase transition relates to various issues: cement-based materials in civil engineering (Baroghel-Bouny et al., 1999), woods in the building industry (Santos 00), plants in botanic (Kozlowski et al., 2002), soils in soil science (Chertkov 02), gels in physical chemistry (Smith et al., 2004), vegetables in foods engineering (Ratti 94), tissues in biomechanics (Gusnard et al., 1977), etc. In civil engineering various concerns are attached to confined phase transitions. The drying shrinkage of materials can induce cracks and enhance the penetration of aggressive agents in concrete structures (Bazant et al., 1982). The crystallization of sea-salts induced by successive imbibition-drying cycles is recognized as being an important weathering phenomenon in dry environments close to the sea (Evans 69). It often leads to serious deterioration in porous sedimentary rocks used for building in coastal areas (Cardell et al., 2003, Fassina 00). Besides, the delayed formation of ettringite crystals, which may be encountered in cement-based materials after hardening (Taylor et al., 2001), can seriously damage concrete structures. Furthermore, the durability of water-infiltrated materials subjected to frost action is a major concern in cold climates (Pigeon et al., 1995). Ice formation in concrete is the cause of billions of euros in damage undergone by concrete structures, even in temperate regions: in 1980 the supervision of French civil engineering works concluded that most damage experienced by buildings, bridges, etc. was originated by frost action (LCPC 03). A better understanding of the mechanics of the liquid-gas phase transition and the liquid-solid phase transition in confined conditions within deformable porous materials could help to improve the resistance of building materials in environmental conditions and, thereby, reduce maintenance and repair costs.

The mechanism of drying shrinkage induced by isothermal evaporation is well known. When a porous material is subjected to an outer relative humidity smaller than its initial inner relative humidity, the thermodynamic vapour imbalance enforces the porous material to exchange water vapour with the outer atmosphere, so that the outer relative humidity progressively settles within the material. In turn the liquid water simultaneously evaporates in order to maintain the vapour-liquid equilibrium. This causes the decrease of the liquid saturation degree. The shrinkage of the porous material finally results from the liquid de-pressure induced at the gas-liquid water interface by the de-saturation process. While the drying kinetics is governed by transport phenomena (Mainguy et al., 2001), the asymptotic drying shrinkage is governed by the outer relative humidity only, since, asymptotically, the air pressure recovers the atmospheric pressure value. Through the years the macroscopic modelling of the drying shrinkage has been addressed this way by many authors (Bazant et al., 1982, Coussy et al., 1998).

At first sight it might be thought that the mechanics of freezing porous materials is similar to that of a sealed water-filled bottle subjected to the frost action, where
the pressure build up and the consecutive failure result only from the undrained 9% expansion of liquid water solidifying within a single large pore. Unfortunately that is not that straightforward. Indeed, cement pastes can still slightly expand if the saturating liquid water is replaced by benzene, which, unlike water, contracts when solidifying (Beaudoin et al., 1974). One of the main causes of this unexpected expansion is the cryosuction process, which drives liquid water from the remaining solution to the crystallized sites (Everett 61). In contrast, water-saturated porous materials can exhibit a contraction if air-voids are present (Piltner et al., 2000). These observations bring to light that the mechanics of confined crystallization within a porous solid does involve the material micro-structural properties, and particularly the pore size distribution, so that a global approach in the context of the mechanics of porous solids has to be worked out (Coussy 05, Coussy et al., 2007, Coussy et al., 2008a). Although drying and crystallization are two quite distinct phenomena, the main purpose of this paper is to show how the physical mechanics of confined phase transitions occurring within a porous solid can be addressed in a unique framework.

2. Phase Transition within a Porous Solid

2.1. Phase equilibrium laws

Since the celebrated works of Gibbs (Gibbs 1899) it is well known that the coexistence of two phases of the same substance requires their specific chemical potential to be equal. Owing to the very definition of the specific (per mass unit) chemical potential $\mu$ related to any phase J, the free energy supply to the phase during the formation of the new mass $dm$ is $\mu_J dm$. Conversely the loss in free energy undergone by the phase K, during the extraction of the same mass $dm$, is $-\mu_K dm$. If we assume that the J-K phase transition occurs with no dissipation, the free energy balance must be zero, resulting in the equality of the specific chemical potential related to each phase in the form

$$\mu_J = \mu_K$$

(1)

If the two coexisting phases J and K are the liquid phase, assumed to be poorly compressible, and the vapour phase, assumed to be an ideal gas, the equilibrium relation (1) provides the celebrated Kelvin’s law, reading

$$p_L - p_{atm} = \rho_L r T \ln h_R$$

(2)

where $p_{atm}$, $h_R$ and $\rho_L$ are respectively the atmospheric pressure, the relative humidity and the volumetric mass of phase J, while $T$ and $r = R/M$ are respectively the absolute temperature and the ratio of the ideal gases constant $R$ per the liquid molar mass $M$. 
When the phase coexisting with the liquid is the solid phase (index \( J = C \), with \( C \) for Crystals), the derivation of the phase equilibrium relation needs further attention because of the non-hydrostatic stress state that a stressed solid is apt to support at rest, and of the elastic energy it can store. Indeed the law governing the liquid-solid equilibrium is still a matter of debate (Sereka et al., 2004). The key point is the determination of the expression related to the chemical potential \( \mu_0 \) of an elastic solid phase \( J \), either solid or liquid. As previously defined the free energy supply \( \mu_0 dm \) associated with the formation of the mass \( dm \) within the phase \( J \) can be split in two terms according to

\[
\mu_0 dm = A_J dm + dW, \tag{3}
\]

In (3) the first term \( A_J dm \), where \( A_J \) stands for the specific Helmholtz free energy, is the free energy supplied to the phase \( J \) by advection, owing to the additional mass \( dm \) that the phase will ultimately contain at the end of the formation process. The second term \( dW \) accounts for the additional work to be done against the already existing phase \( J \) to make room for the infinitesimal mass in formation within the phase. In order to determine \( dW \) let then the index 0 refer to an undeformed (and unstressed) reference state. For instance, the mass \( dm \) occupies the volume \( dV_0 = dm/\rho_0 \) in the undeformed reference state, whereas it occupies the volume \( dV = dm/\rho_1 \) in the deformed current state. The distinction between the reference undeformed state and the current deformed state allows us to split the work \( dW \) in two terms according to

\[
dW = dW_{0 \rightarrow dV_0} + dW_{dV_0 \rightarrow dV}, \tag{4}
\]

where \( dW_{0 \rightarrow dV_0} \) accounts for the work done against the already existing phase \( J \) to make room for the undeformed volume \( dV_0 = dm/\rho_0 \) that the mass \( dm \) would occupy prior to any deformation; \( dW_{dV_0 \rightarrow dV} \) accounts for the additional work done against the phase \( J \) in order that the volume \( dV_0 \) deforms into the volume \( dV \) that the mass \( dm \) will finally occupy in the current strain state of phase \( J \). The work \( dW_{dV_0 \rightarrow dV} \) is thereby simply equal to the opposite of the strain work undergone by the mass occupying initially the volume \( dV_0 \) and transforming into the volume \( dV \). Let then \( \sigma_i \) and \( s_i \) be respectively the mean stress and the deviatoric stress tensor. Let also \( \varepsilon_i \) and \( e_i \) be respectively the current volumetric strain and the current deviatoric strain tensor related to phase \( J \) with respect to the reference state. In infinitesimal transformations both

\[
\varepsilon_i = (1/\rho_j - 1/\rho_{0j})/(1/\rho_0)_i
\]

and the norm of \( e_i \) are much smaller than 1. Owing to their definitions, works \( dW_{0 \rightarrow dV_0} \) and \( dW_{dV_0 \rightarrow dV} \) can then be expressed in the respective forms
Collecting the results (3)-(6) we finally get $\mu_0$ in the form

$$
\mu_j = A_j - \sigma_j/\rho_{j0} - (\sigma_j \epsilon_j + s_j : e_j)/\rho_{j0} \tag{7}
$$

In linear elasticity $A_j$ is the sum of a linear form and a quadratic form of its arguments $T$, $1/\rho_j$ and $e_j/\rho_{j0}$, while $\sigma_j$ and $s_j$ are linear functions of the variations of the latter. As a result $\mu_0$ is the sum of a linear form and of a quadratic form of its natural arguments $T$, $\sigma_j$ and $s_j$. In infinitesimal transformations the quadratic terms related to the stress components are second order terms with regard to the linear terms. Besides, when addressing the liquid-solid phase equilibrium, it is convenient to adopt for the reference state of both phases the melting temperature $T_m$ related to the phase equilibrium which is achieved when both phases are at atmospheric pressure in the absence of any shear. For an isotropic solid ($J = C$), omitting the subscript $J$ for the stress components, neglecting the quadratic terms both with regard to the stress contribution and with regard to the relative temperature variation $(T_m - T)/T_m$, this choice for the reference state finally provides

$$
\mu_C = \mu_{C0} - (\sigma_C + p_{\text{atm}})/\rho_{C0} - (T - T_m)s_{C0}
$$

$$
\mu_L = \mu_{L0} + (p_L - p_{\text{atm}})/\rho_{L0} - (T - T_m)s_{L0} \tag{8}
$$

where $s_j$ is the specific entropy related to phase $J$. At the melting point, where $T_m - T$ and $\sigma_j + p_{\text{atm}}$ are zero, the liquid-solid phase equilibrium relation (1) requires the reference chemical potentials to be equal, resulting in $\mu_{C0} = \mu_{L0}$. When the temperature drops below the melting temperature $T_m$, combining (1) and (8) for $J = L$ or $C$ and making the approximation

$$
\rho_{L0}/\rho_{C0} - 1 = 1 - \rho_{C0}/\rho_{L0} = 0.09 \text{ for water} << 1 \tag{9}
$$

we finally find out that the liquid phase and the solid phase can co-exist provided that they are pressurized according to

$$
-\sigma_C - p_L = \Delta S_m (T_m - T) \tag{10}
$$

where $\Delta S_m$ is the volumetric melting entropy defined by

$$
\Delta S_m = \rho_{C0}(s_{L0} - s_{C0}) \tag{11}
$$

when the solid crystal phase is subjected to a hydrostatic stress state, so that $\sigma_C = -p_C$ (10) reduces to the standard Thomson law (Markov 03), reading
\[ p_c - p_L = \Delta S_m (T_m - T) \]  

(12)

### 2.2. In-pore phase transition

The previous section has analysed the general conditions governing a phase transition. This section addresses the case where the phase transition occurs within a rigid porous solid, leaving to the next section the case of a deformable porous solid. First considering the liquid-vapour phase transition, dry air is assumed to freely penetrate the porous volume where the phase transition occurs. At any time the porous volume is therefore filled up by the liquid and by the gas (index \( J = G \)) consisting of dry air and of vapour in equilibrium with the liquid. Let then \( \phi_0 \) and \( \phi_i \) be respectively the initial porosity and the current partial porosity related to the phase \( J \), and let \( S_L \) and \( S_G \) be the liquid and gas saturations accounting for the fractions of the porous volume occupied by the liquid and by the gas. Owing to the assumed rigidity of the porous solid, we have

\[ \phi_L = \phi_0 S_L, \quad \phi_G = \phi_0 S_G, \quad S_L + S_G = 1 \]  

(13)

Let in addition \( p_J \) be the pressure related to phase \( J \), and let \( F \) be the free energy of the porous solid once the bulk phases \( L \) and \( G \) have been removed. Assuming no hysteretic capillary effect the first law and the second law of the thermodynamics combine to the isothermal incremental free energy balance (Coussy 04)

\[ p_L d\phi_L + p_G d\phi_G - dF = 0 \]  

(14)

Since the bulk liquid and gas phases have been removed, and that the porous solid is assumed to be undeformable, the free energy \( F \) reduces to the surface energy of the interfaces between the phases and the solid matrix forming the solid part of the porous solid. Denoting by \( U \) the surface energy per unit of porous volume this allows us to write

\[ F = \phi_0 U \]  

(15)

Substituting (13) and (15) in (14) we get

\[ p_G - p_L = -dU / dS_L \]  

(16)

which shows that the liquid saturation \( S_L \) is a state function of the capillary pressure \( p_G - p_L \). We write

\[ S_L = \sigma (p_G - p_L) \]  

(17)
where \( \sigma \) is the so-called capillary curve. The macroscopic capillary curve can receive a simple microscopic interpretation at the pore scale. At that scale the mechanical equilibrium of the current gas-liquid interface is governed by Laplace’s law. As a result, assuming a zero wetting angle and assuming the liquid to be the wetting fluid, we write

\[
p_{\text{atm}} - p_L = 2\gamma_{GL} / r
\]

where \( \gamma_{GL} \) is the energy per unit of surface of the gas-liquid interface, whose \( r \) is the mean curvature radius. Standard porosimetry then provides the cumulated porous volume fraction \( S(r) \) of pores having a pore entry radius smaller than \( r \), or, equivalently, the cumulated porous volume fraction \( 1 - S(r) \) of pores having a pore entry radius greater than \( r \). This is illustrated in the left side of Fig. 1 for a cement paste. For a given value of the capillary pressure \( p_G - p_L \), the pores with an entry radius smaller than that given by (18) will still remained filled by the liquid while the other pores with larger entry radius will be invaded by the gas. As a consequence we write

\[
S_L = S(r)
\]

Figure 1. Left hand: cumulative pore volume fraction \( 1 - S(r) \) of pores having a pore entry radius greater than \( r \) for a typical cement paste from porosimetry data extracted from literature (Cheng-yi et al., 1985). Right hand: cooling \( \Delta T = (T - T_m) \) and relative humidity \( h_R \) plotted against the liquid saturation \( S_L \) as predicted by (24) and (21) for the experimental data of the left hand figure.

Combining (18) and (19) we get

\[
S_L = S\left(2\gamma_{GL} / (p_G - p_L)\right)
\]
which provides an explicit determination of the capillary curve. If in addition we 
assume that the gas remains constantly at the atmospheric pressure $P_{\text{atm}}$ of Kelvin’s 
law (2) and (20) finally combine to give

$$S_L = S\left(-2\gamma_{CL}/P_L r T \ln h_R \right)$$  \hspace{1cm} (21)

which provides the liquid saturation $S_L$ as a function of the current relative humidity $h_R$.

Similarly to the relation linking the liquid saturation $S_L$ to the current relative 
humidity $h_R$ we found for the liquid-vapour transition, it is tempting to look for an 
alogous relation linking the liquid saturation $S_L$ to the current cooling $T_m - T$ for 
the liquid-solid phase transition. To that purpose we first replace (18) by

$$p_c - p_L = 2\gamma_{CL} / r$$  \hspace{1cm} (22)

where $\gamma_{CL}$ is the interface energy of the liquid-solid interface and $r$ its curvature 
radius as illustrated in right hand of Fig. 2. As result, instead of (21) we now find

$$S_L = S\left(2\gamma_{CL} / (p_c - p_L) \right)$$  \hspace{1cm} (23)

which, combined with Thomson’s law (12), provides the liquid saturation $S_L$ as a function of the current cooling $T_m - T$ in the form

$$S_L = S\left(2\gamma_{CL} / \Delta S_m (T_m - T) \right)$$  \hspace{1cm} (24)
However, instead of the hydrostatic stress state and the curved solid-liquid interface represented in the right hand of Fig. 2, the phase equilibrium law (10), when associated with the same cooling, allows the stress state to be non-hydrostatic and the interface to be flat, as represented in the left hand of Fig. 2. The key relation (24) would then no longer be valid. Fortunately it can be shown (Coussy et al., 2008c) that the non-hydrostatic stress state associated with the flat interface is not stable. Indeed, for the same cooling the free Helmholtz energy associated with a flat interface is larger than the one associated with a curved interface because of the additional shear contribution to the elastic energy in the former case. As a result the flat solid-liquid interface corresponding to a non-hydrostatic stress state will inexorably transform into a curved interface corresponding to a hydrostatic stress state, so that (24) finally applies. Based on relations (21) and (24) we have just derived, the right hand of Fig. 1 shows the liquid saturation $S_L$ as a function of both the relative humidity $h_R$ and the cooling $T_m - T$ when the liquid is water and for the cement paste corresponding to the experimental data reported in the right hand of Fig. 1.

3. Unsaturated Poroelasticity

According to the analysis of the previous section, two phases of the same substance which co-exist in a porous space are not subjected to the same pore pressure. Accordingly the prediction of drying shrinkage of elastic porous solids, or that of the deformation due to their freezing, requires the extension of saturated poroelasticity to unsaturated conditions where the internal solid walls delimiting two separate parts of the porous space are not subjected to the same pressure. This is the topic of this section.

3.1. State equations of unsaturated poroelasticity

Let us consider a porous solid which is now deformable and whose porous space is saturated both by a liquid phase (index L) and by a phase either gaseous or solid (index $J = G$ or C). Noting $\sigma_{ij}$ and $\varepsilon_{ij}$ the overall stress and strain components, the free energy balance (14) extends in the form

$$\sigma_{ij} \, d\varepsilon_{ij} + p_L \, d\phi_L + p_J \, d\phi_J - dF = 0$$

(25)

where $\sigma_{ij} \, d\varepsilon_{ij}$ accounts for the strain work. Since the porous space now deforms, instead of (13) we now write

$$\phi_L = \phi_0 S_L + \phi_T \quad \phi_J = \phi_0 S_J + \phi_T \quad S_L + S_J = 1$$

(26)
where \( \phi_l \) accounts for the change in the partial porosity \( \phi_l \) due the deformation only. Note that saturation \( S_j \) can be coined as a Lagrangian saturation related to phase \( J \) since it refers to the undeformable configuration. More precisely, starting from fully liquid saturated conditions, \( \phi_0 S_L \) is the fraction of the porous volume in the non deformed configuration whose solid walls will be still wetted by the liquid in the current deformed configuration (Coussy 05, Coussy 07).

With regard to the undeformable porous solid the free energy \( F \) of the deformable system obtained by removing the bulk phases \( L \) and \( J \) now splits into the surface energy \( \phi_0 U \) associated with the interfaces, and the elastic energy \( \Psi_S \) stored in the deformable solid matrix. Accordingly expression (15) transforms into

\[
F = \phi_0 U + \Psi_S
\]  

(27)

Substitution of (26) and (27) into (25) provides

\[
\sigma_{ij} d\varepsilon_{ij} + p_L d\phi_L + p_J d\phi_J - d\Psi_S - \phi_0 \left[ (p_J - p_L) dS_L + dU \right] = 0
\]  

(28)

The change in \( U \) is mainly due to the creation of new interfaces between the phases during the invasion process by the phase \( J \), \( U \) being slightly affected by the deformation when \( S_L \) is held constant. According to the analysis of the previous section \( U \) can be still considered as a function of the liquid saturation \( S_L \) only. Conversely, if we assume infinitesimal elastic deformations of the porous solid, its elastic energy \( \Psi_S \) will be slightly affected by the variation \( dS_L \) of the liquid saturation. As a result, (28) allows us to conclude that (15) will still hold, while the free energy balance related to the deformable porous solid obtained by removing the interfaces is

\[
\sigma_{ij} d\varepsilon_{ij} + p_L d\phi_L + p_J d\phi_J - d\Psi_S = 0
\]  

(29)

from which we derive

\[
\sigma_{ij} = \frac{\partial \Psi_S}{\partial \varepsilon_{ij}} \quad p_L = \frac{\partial \Psi_S}{\partial \phi_L} \quad p_J = \frac{\partial \Psi_S}{\partial \phi_J}
\]  

(30)

Letting \( W_S = \sigma_{ij} \varepsilon_{ij} + \phi_L p_L + \phi_J p_J - \Psi_S \) be the Legendre transform of \( \Psi_S \) with regard to both \( \phi_L \) and \( \phi_J \) we alternatively get

\[
\varepsilon_{ij} = \frac{\partial W_S}{\partial \sigma_{ij}} \quad \phi_L = \frac{\partial W_S}{\partial p_L} \quad \phi_J = \frac{\partial W_S}{\partial p_J}
\]  

(31)

In the context of both infinitesimal deformation and linear isotropic poroelasticity the expression of the elastic energy of the solid matrix, \( W_S = \Psi_S \), is
\[
W_s = \frac{1}{2K}\left(\sigma + b_L p_L + b_J p_J\right)^2 + \frac{1}{2N_{LL}} p_L^2 + \frac{1}{N_{LL}} p_L p_J + \frac{1}{2N_{JJ}} p_J^2 + \frac{1}{4G} s_{ij} s_{ij}\]  \tag{32}
\]

where \(\sigma = \sigma_{kk}/3\) and \(s_{ij}\) are respectively the mean stress and the components of the deviatoric stress tensor. Letting in addition \(\varepsilon = \varepsilon_{kk}\) be the volumetric strain and substituting (32) in (31) we finally get
\[
\sigma = K\varepsilon - b_L p_L - b_J p_J \quad s_{ij} = 2Ge_{ij}\]  \tag{33}
\[
\varphi_L = b_L \varepsilon + p_L/N_{LL} + p_J/N_{LJ}\]  \tag{34}
\[
\varphi_J = b_J \varepsilon + p_L/N_{LJ} + p_J/N_{JJ}\]  \tag{35}

\(K\) and \(G\) are therefore identified as the bulk modulus and the shear modulus of the dry porous solid which can be recorded in the absence of pore pressures.

When \(p_L = p_J\) we must retrieve the saturated case so that we have (Coussy 91)
\[
b_L + b_J = b = 1 - K/k_s \quad 1/N_{LL} + 2/N_{LJ} + 1/N_{JJ} = 1/N = (b - \phi_0)/k_s \]  \tag{36}

where \(b\) and \(N\) are the poroelastic properties of the porous solid with uniform pore pressure, while \(k_s\) is the bulk modulus of the solid matrix assumed to be homogeneous. Using mesoscopic-macroscopic considerations (Coussy 91, Coussy et al., 2008) or more refined up scaling methods (Dormieux et al., 2006), it can be further shown that
\[
K = L \text{ or } J : \quad 1/N_{KK} + 1/N_{LJ} = (b_K - \phi_0 S_{LJ})/k_s\]  \tag{37}

Provided that \(k_s\) is known the previous relations are independent of the porous solid considered. In contrast separate expressions of the poroelastic properties \(K, G, b_J\) and \(N_{JK}\) as functions of the porosity \(\phi_0\) and saturation \(S_j\) require specific pieces of information on the porous solid considered. This is addressed in the next section.

3.2. Estimates of the unsaturated poroelastic properties

3.2.1. Pore iso-deformation

The first relation of (36) shows that \(b_L\) and \(b_J\) are not independent and allows us to introduce a Bishop-like parameter \(\chi\) (see (Bishop et al. 1963)), depending on the liquid saturation \(S_L\) and such that
\[
b_L = b\chi(S_L) \quad b_J = b[1 - \chi(S_L)]\]  \tag{38}
The explicit determination of function $\chi(S_L)$ needs new pieces of information. Using up scaling procedures, the Bishop-like parameter $\chi$ can be shown to reduce to the liquid saturation $S_L$ provided that the deformation localisation tensor is the same for all pores (Chateau et al., 2002). In fact, without the need of having recourse to such sophisticated procedures, this result can be simply recovered by assuming that all pores undergo the same volumetric deformation (Coussy 07). This assumption amounts to writing

$$ p_L = p_j = 0 : \quad \varphi_L/\varphi_0 S_L = \varphi_j/\varphi_0 S_j $$

Substitution of (39) in (34) and (35) then provides

$$ b_L/S_L = b_j/S_j $$

Substituting (40) in the first of relations (36), we finally get the above mentioned identification, that is

$$ b_L = b S_L \quad b_j = b (1 - S_L) \quad \chi = S_L $$

Because of relations (37) and (41), it can be then shown that the porous volumes occupied by the liquid L and the phase K would still deform in the same manner provided that they are subjected to the same pressure.

### 3.2.2. Mori-Tanaka scheme

When the pore iso-deformation assumption is relevant, we are left with the determination of the expressions of the bulk modulus $K$ and the shear modulus $G$ as functions of the porosity $\phi$. This determination can be achieved by using up scaling procedures. It is no question here to enter the details of these procedures, the reader being referred to (Dormieux et al., 2006) for a comprehensive application of micromechanics to porous materials. In this section we will restrict ourselves to recall well known results associated with the Mori-Tanaka scheme.

Since the overall volumetric strain $\varepsilon$ is the average of the volumetric strain, letting $\varepsilon_s$ be the volumetric strain of the solid matrix we first write

$$ \varepsilon = (1-\phi_0) \varepsilon_s + \varphi_L + \varphi_j $$

The variation of volume $\varphi_K V$ of a spherical void of initial volume $\phi_0 S_K V$, which is embedded within an elastic matrix with $k$ and $g$ as bulk and shear moduli, while subjected to the pore pressure $p_K$, can be expressed in the form
\[ \varphi_k / \varphi_0 S_k = (1 + 3k / 4g) \varepsilon_0 + 3p_k / 4g \]  

(43)

where \( \varepsilon_0 \) is the volumetric strain prescribed at infinity. The homogenization schemes differ from each other by the choice of the embedding medium having the elastic properties \( k \) and \( g \). The Mori-Tanaka scheme consists of choosing the solid matrix as the embedding medium, that is choosing \( k = k_S \) and \( g = g_S \), resulting in \( \varepsilon_0 = \varepsilon_S \). The self-consistent scheme consists of choosing the porous solid whose we look for poroelastic properties as the embedding medium, that is choosing \( k = K \) and \( g = G \). In the following we will restrict to the former choice so that (43) becomes

\[ \varphi_k / \varphi_0 S_k = (1 + 3k_S / 4g_S) \varepsilon_S + 3p_k / 4g_S \]  

(44)

Substitution of (44) for successively \( K = L \) and \( K = J \) into (42) provides \( \varepsilon_S \) in the form

\[ \varepsilon_S = \frac{4g_S}{3\phi_0 k_s + 4g_S} \left[ \varepsilon - 3\phi_0 [S_L p_L + S_J p_J] / 4g_S \right]. \]  

(45)

In turn, substituting (45) in (43) we recover the constitutive equations (34) and (35) of unsaturated poroelasticity and the associated relations (36)-(37), but now with the benefit of the new relations

\[ b_L = bS_L \quad b_J = b(1 - S_L) \quad K = 4k_S g_S (1 - \phi_0) / (3\phi_0 k_s + 4g_S) \]  

(46)

\[ 1 / N_{kk} = S_k^2 (1 / N - 3\phi_0 / 4g_s) + 3\phi_0 S_k / 4g_s \]

\[ 1 / N_{LJ} = S_L S_J (1 / N - 3\phi_0 / 4g_s) \]

The determination of the relations providing the missing relation involving the shear modulus \( G \) is by far less straightforward since it corresponds to prescribe at infinity the deviatoric strain instead of the volumetric strain. We will restrict here to recall the final result (see for instance (Dormieux et al., 2006))

\[ G = \frac{(1 - \phi_0) [9k_S + 8g_S] g_S}{9k_S [1 + 2\phi_0 / 3] + 8g_S [1 + 3\phi_0 / 2]} \]  

(47)

3.2.3. Beyond the pore iso-deformation assumption

The comparison of the two first relations in (46) with (41) shows that the pore iso-deformation holds when adopting the Mori-Tanaka scheme. This is due to the fact that all pores see the same embedding medium irrespective of their size, with thereby no associated scale effect. To roughly account for this scale effect, it can be first considered that there are only two sizes of pores referred to by subscript J
(= G or C) for the largest pores occupied by the non wetting gas or the solid crystal phase, and by subscript L for the smallest pores occupied by the wetting liquid, in conformity with the analysis we did in the first section. This rough scale separation, which is actually quite approximate since the smallest pores occupied by the gas or the solid crystals have a size comparable with the largest pores occupied by the liquid, leads us to develop a two-scale scheme where we write

\[
b_j = 1 - K / \kappa_j \quad 1/ N_{jj} = (b_j - \phi_0 S_j) / \kappa_j
\]  

(48)

where \( \kappa_j \) is the bulk modulus of the porous solid matrix consisting of the original solid matrix and of the smaller pores forming the porous volume at pressure \( p_L \). The porosity \( \phi_0^J \) of this porous solid matrix is the ratio of the porous volume at pressure \( p_L \) to the overall volume from which we remove the porous volume at pressure \( p_j \). Accordingly we write

\[
\phi_0^J = \phi_0 S_L / (1 - \phi_0 S_j)
\]  

(49)

Owing to the general relation (37) the other poroelastic properties are then derived from the sequence

\[
b_L = b - b_j = K / \kappa_j - K / k_S
\]

\[
1/ N_{LL} = (b_L - \phi_0 S_L) / k_S - (b_j - \phi_0 S_j) / \kappa_j
\]

\[
1/ N_{LJ} = (b_L - \phi_0 S_L) / k_S - 1/ N_{JJ}
\]  

(50)

The assessment of the poroelastic properties needs the determination of \( \kappa_j \), which can be achieved by using a specific homogenization scheme. However the two-scale approach does not affect the results we already derived, when using the Mori-Tanaka scheme. Indeed it can be easily checked that the pore iso-deformation condition \( b_j = bS_j \) is preserved when using (50) and the expression of \( \kappa_j \) associated with the Mori-Tanaka scheme and obtained by replacing \( K \) and \( \phi_0 \) respectively by \( \kappa_j \) and \( \phi_0^J \) in the second relation in (46).
A more refined homogenization scheme is the differential homogenization scheme sketched out in Fig. 3. Whatever the value of \( r \) the differential scheme consists of considering only the pores occupying the fraction \( \phi_0 dS(r - dr) \) as forming the porous space related to the porous solid that the larger pores occupying the volume fraction \( \phi S(r) \) see as embedding medium. Similarly to (49) the porosity \( d_0 \) of the embedding medium is then given by

\[
d_f = \phi_0 dS / (1 - \phi_0 S)
\]  

In view of the explicit determination of the unsaturated poroelastic properties further calculations let then first rewrite (46) and (47) in the form

\[
K/k_S = 1 - \phi_0 (1 + 3K/4G) \quad G/g_S = 1 - 5\phi_0 (1 + 4G/3K) / (3 + 8G/3K)
\]  

Applying (52), where we replace \( K, G, k_S, g_S \) and \( \phi_0 \) by respectively \( \kappa, \gamma, \kappa + d\kappa, \gamma + d\gamma \) and \( d_0 \), and retaining only the terms of main order with regard to \( d\kappa, d\gamma \) and \( dS \) we finally get

\[
\frac{d\kappa}{\kappa} = \frac{\phi_0 dS}{1 - \phi_0 S} \times \frac{3\kappa + 4\gamma}{4\gamma} \quad \frac{d\gamma}{\gamma} = \frac{5\phi_0 dS}{1 - \phi_0 S} \times \frac{3\kappa + 4\gamma}{9\kappa + 8\gamma}
\]  

Let then \( a \) be defined by

\[
a = 4\gamma / 3\kappa
\]  

so that
\[
d a/a = d\gamma / \gamma - d\kappa / \kappa
\]  \hspace{1cm} (55)

From (53)-(55) we derive
\[
\int_{a(S_j)=4\gamma_j/3\kappa_j}^{a(S_j) = 4\gamma_j/3\kappa_j} \left(3 + 2a\right)/3 \left(a^2 - 1\right) da = \int_{S_j} \phi_0 dS / (1 - \phi_0 S)
\]  \hspace{1cm} (56)

which can be integrated in the form
\[
\left|1 - a(S_j)\right|^5 \left[\left|1 + a(S_j)\right|^{-1} - 1 + a_s\right]^{-1} \left(1 + a_s\right)^{-1} (1 - \phi_0)^6 (1 - \phi_0 S_j)^{-6}
\]  \hspace{1cm} (57)

From (53) and (55) we get
\[
d\kappa / \kappa = (3 + 2a) da / 3a (a - 1)
\]  \hspace{1cm} (58)

Integrating the left hand side between \(k_S\) and \(\kappa_j\) and the right hand side between \(a_S\) and \(a(S_j) = 4\gamma_j/3\kappa_j\), we successively obtain
\[
\kappa_j / k_S = \left|1 - a(S_j)\right|^5 \left|\left|1 + a(S_j)\right|^{-1} - 1 + a_s\right|^{-5/3} a_s^{-1} (S_j)
\]  \hspace{1cm} (59)

\[
K / k_S = \left|1 - a(0)\right|^5 \left|\left|1 + a(0)\right|^{-1} - 1 + a_s\right|^{-5/3} a_s^{-1} (0)
\]

and
\[
\gamma_j / g_s = \left|1 - a(S_j)\right|^{5/3} \left|\left|1 + a(S_j)\right|^{-1} - 1 + a_s\right|^{-5/3} G / g_s = \left|1 - a(0)\right|^{5/3} \left|\left|1 + a(0)\right|^{-1} - 1 + a_s\right|^{-5/3}
\]  \hspace{1cm} (60)

Finally, since \(b = 1 - K/k_S\) (48), (50) and (59) combine to
\[
b = 1 - \left|1 - a(0)\right|^{5/3} \left|\left|1 + a(0)\right|^{-1} - 1 + a_s\right|^{-1} (0)
\]
\[
b_j = 1 - \left|1 - a(S_j)\right|^{5/3} \left|\left|1 + a(S_j)\right|^{-1} - 1 + a_s\right|^{-1} (0)
\]
\[
b_L = \left|1 - a(0)\right|^{5/3} \left|\left|1 + a(0)\right|^{-1} - 1 + a_s\right|^{-1} \left|1 - a(1 - S_L)\right|^{-5/3} \left|\left|1 + a(1 - S_L)\right|^{-1} - 1 + a_s\right|^{-1} (0)
\]  \hspace{1cm} (61)

Although no simple expression can be obtained for \(\chi\) defined by (38), expression (61) of Biot coefficients related to the differential scheme shows that relation (41) no more holds. Indeed the pores do not undergo the same volumetric deformation owing to the coupling between of the deformation of pores having distinct sizes. The remaining poroelastic properties \(N_{jk}\) are then provided by substituting (59) and (61) into their expressions (50).
In Fig. 4, adopting the value 0.3 for both the Poisson coefficient $\nu_S$ and the porosity $\phi_0$, we plotted the Bishop-like parameter $\chi$ and the various poroelastic coupling properties $g_S/N_{JK}$ against the liquid saturation $S_L$ for both the Mori-Tanaka scheme and the differential scheme. In the differential scheme the larger pores deform more than the smaller ones so that $\chi$ exhibits a lower value than the liquid saturation $S_L$ which is the value associated with pore iso-deformation. Furthermore, in the absence of pore iso-deformation the poroelastic coupling properties $g_S/N_{JK}$ are not symmetric with regard to the line $S_L/2$ properties $g_S/N_{LL}$ and $g_S/N_{LJ}$ reaching their maximum value for values larger than $S_L = 1/2$ with the opposite for $g_S/N_{JJ}$.

4. Drying shrinkage and freezing expansion

When an initially liquid-saturated porous solid is subjected to surroundings of decreasing relative humidity, it shrinks. Indeed, as captured by (21) the pore entry radius, and consequently the liquid saturation $S_L$, have to adjust to the current relative humidity in order that the confined liquid water to remain in thermodynamic equilibrium with the current vapour pressure imposed by the current relative humidity. This is accompanied with a depressurization of the remaining liquid water, which in turn provokes a drying shrinkage. When an initially liquid-saturated porous solid is subjected to a decreasing temperature of the surroundings, it generally expands. As indicated in the introduction, experiments performed on benzene-saturated cement pastes have even shown that the expansion still occurs even though the saturating liquid contracts when solidifying (Beaudoin et al., 1974). This apparent paradoxical expansion can now be explained as follows. As the temperature $T$ decreases below the melting point $T_m$, according to (12) the crystal pressure $p_C$ has to increase within the already frozen part of the porous volume whose extension is governed by (24). This crystal pressure increase is achieved by
the further freezing of some extra liquid water entering the already frozen zone after having been driven from the remaining liquid solution. This is the so-called cryosuction effect. The purpose of this section is to show how both the drying shrinkage and the freezing expansion caused solely by the cryosuction effect can be both addressed by unsaturated poromechanics.

Consider then a stress-free drying process so that $\sigma = 0$, starting from a reference initial state where the porous material is saturated ($S_L = 1$) the pore pressure is atmospheric ($p_L = p_{atm}$) and the relative humidity is 100%. With regard to a zero pore pressure state, the deformation $\varepsilon_0$ related to the drying initial state is provided by substituting the initial conditions in (33) with $b_L = b$ and $b_J = 0$ so that

$$\varepsilon_0 = b p_{atm}/K$$

(62)

When the relative humidity is lowered below 100% and the gas pressure is maintained at atmospheric pressure $p_{atm}$ a drying shrinkage of intensity $\varepsilon_{\text{drying}} = -\Delta \varepsilon - \varepsilon_0$ is observed. Its intensity is obtained by substituting $\sigma = 0$, (2) and (38) in (33) and using (62). With the help of the same equations the intensity of the extra elastic energy $W_{\text{drying}} = W(\varepsilon) - W(\varepsilon_0)$, which is stored during the drying process, can be derived from (32). We get

$$\varepsilon_{\text{drying}} = \left( b \frac{\chi}{K} \right) \left( p_0 - p_L \right) = \rho_L r T \left( b \frac{\chi}{K} \right) \ln h_R$$

(63)

$$W_{\text{drying}} = \left( b^2 (\chi)^2 / 2K + 1/2 N_{LL} \right) \left( \rho_L r T \ln h_R \right)^2$$

Consider now a freezing process with the same initial conditions, but the liquid now being the phase maintained at atmospheric pressure. Letting Thomson’s law (12)
and the crystal pressure $p_C$ play the role of respectively Kelvin’s law (2) and the gas pressure $p_G$ in the previous development which has lead to (63), we similarly get

$$\varepsilon_{\text{cryosuction}} = \left( b (1 - \chi) / K \right) (p_C - p_L) = \left( b (1 - \chi) / K \right) \Delta S_m (T_m - T)$$

$$W_{\text{cryosuction}} = \left( b^2 (1 - \chi)^2 / 2K + 1 / 2N_{CC} \right) (\Delta S_m (T_m - T))^2$$

(64)

It becomes then quite similar to analyse the drying shrinkage or the volumetric deformation induced by cryosuction. Indeed, using a specific homogenization scheme the poroelastic properties $b$, $K$, $\chi$ and $N_{LL}$ or $N_{CC}$ are then known as a function of the porosity $\phi$, the current liquid saturation $S_L$ and the matrix elastic properties $k_S$ and $g_S$. In addition the current liquid saturation $S_L$ is known as a function of the pore size distribution and either the current relative humidity $h_R$ or the cooling $T_m - T$ through (21) or (24), according to the phase transition considered.

For the cement paste corresponding to the experimental data reported Fig. 1, we plotted in Fig. 5 the volumetric deformation $\varepsilon_{\text{drying}}$ and the elastic energy $W_{\text{drying}}$ against $S_L$ for both the Mori-Tanaka scheme and the differential scheme. The deformation induced by the phase transition exhibits a peak which is achieved when the increase of the difference of pressure becomes compensated by the decrease of the extent of the still wetted porous volume and the associated decrease of the Bishop-like parameter $\chi$. As shown in Fig. 5 the drying shrinkage is the most significant for the differential scheme because the latter accounts for the softening of the material induced by the difference of deformation of pores having a different size. Similarly the elastic energy stored in the solid matrix during the drying process is more significant for the differential scheme. As a result the difference of deformation of pores having a different size can significantly effect the strength of a porous material subjected to drying if its fracture is brittle and ultimately governed by a threshold in the elastic energy that the solid matrix can store.

5. Conclusion

In this paper we have shown that the mechanics of confined phase transition within a deformable porous solid can be addressed in a unique framework whatever the phase transition considered, either liquid-gas in the case of the drying of porous materials or liquid-solid in the case of their freezing. Indeed, owing to stability considerations a hydrostatic stress will ultimately prevail within the solid crystal phase so that the latter behaves like a compressible elastic fluid as long as only in-pore phase transition is involved. The extension of saturated poroelasticity to unsaturated conditions has allowed us to work out appropriate constitutive equations to capture the deformation resulting from in-pore phase transition within an elastic porous solid, while the use of homogenization schemes has provided estimates of the unsaturated poroelastic these constitutive equations involve. The prediction of the deformation
induced by the phase transition has then shown the significant effect of the pore size distribution, since the intensity of the deformation as well as that of the elastic energy that the solid matrix can store strongly depends upon the homogenization scheme. As developed in (Coussy 06) this analysis can be easily extended to address the drying-induced crystallization of sea salts, which combines the two phase transitions explored in this paper. However the improvement in the accuracy of the analysis needs further refinements since it is must be recalled that it is based upon a rough scale separation between the sizes of the pore volumes invaded by the two phases. In addition the progressive cracking of the solid matrix under the internal stresses generated by the drying process might significantly alter the conclusions drawn from a poroelastic reversible analysis. Further research is thereby needed to assess the effects of the size of the pores upon the ultimate strength of porous materials subjected to confined phase transitions, using the tools provided by microporomechanics (Dormieux et al., 2006). In addition, in the analysis of the drying and the freezing of non cohesive porous materials like soils, use of the extension of unsaturated poroelasticity to unsaturated poroplasticity will certainly prove to be fruitful (Coussy et al., 2008b). Besides, the results obtained in this paper have been derived by using a macroscopic approach to in-pore phase transition. This rather simple general approach needs a further confirmation by performing more advanced molecular simulations applied to crystallization processes (Denoyel et al., 2002), which will allow us to account for specific pore geometries and realistic intermolecular interactions related to the solidifying substance and the surrounding solid matrix.

6. Acknowledgements

The author acknowledges the support of the ATILH-CNRS research program "Porosity, Transport, Strength".

7. References


