# Mechanics and Physics of Porous Solids

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Based on a lecture from O. Coussy and M. Vandamme





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### The unsaturated solid



An unsaturated solid is a porous medium whose porosity is filled by more than one distinct phase:

- $\bullet \mbox{ drying rock/wet sand} \ldots \rightarrow \mbox{ air and } water$
- $\bullet~{\rm freezing/thawing~rock}$   $\rightarrow$  water and ice
- $\bullet\,$  oilfield  $\rightarrow\,$  oil, water and gas
- . . .

What are the changes induced in the poroelasticity and the transport laws by the presence of these multiple phases ?

# Surface energy



A molecule at an interface has a higher energy than a molecule in the bulk (less stabilizing interactions). We can then define a surface energy  $\gamma$  defined as half the excess energy obtained by dividing an homogeneous solid in 2 parts creating a surface.

### $dW = 2\gamma dA$

# Surface stress and surface energy





For a fluid surface as the molecule are mobile any change of the surface area leads to a change of the number of molecules at the surface. For a solid surface, any change of area corresponds to a stretching of the bonds at a constant number of molecules.

Surface energy  $\Leftrightarrow$  Surface stress

Surface energy  $\neq$  Surface stress Shuttleworth equation:  $\gamma^* = \gamma + \frac{d\gamma}{dc}$ 

 $d\epsilon = \frac{dA}{A}$  is called the surface strain

# Wettability and contact angle



#### Young-Dupré law

We can define the spreading parameter as  $S = \gamma_{GS} - (\gamma_{LS} + \gamma_{GL})$ .

- If S > 0 the liquid will wet the surface (energetically favorable) and we will be in the case of perfect wetting.
- If S < 0 the quality of wetting can be characterized by a contact angle following Young-Dupré law

$$\gamma_{\textit{GS}} = \gamma_{\textit{LS}} + \gamma_{\textit{GL}} \cos heta$$

The demonstration of this law is made with the projection of surface forces on the triple line (the line where all phases are in contact)

# Wettability of natural rocks

#### Water-wet/oil-wet

Aqueous solutions and oil products don't have the same behavior with solids. Water has a high surface energy ( $\approx$  70 mJ/m<sup>2</sup>) because of the hydrogen bonds Organic products (made from carbon chains, alcanes...) have a low surface tension (London interaction)





#### Water-wet and Oil-wet

Some solids will be wet by aqueous solutions (water-wet or hydrophilic) and others will be wet by organic compounds (oil-wet or hydrophobic). A same solid cannot be wet by the two kinds of liquids, but a same solid can be non-wet for both (Teflon products)

# Wettability of natural rocks

#### Ususally natural rocks are water-wet

Natural rocks are formed by minerals which are water-wet so most of the natural rocks are water-wet.

For a rock in contact with oil and petroleum products, adsorption of molecules (asphaltenes) can make them oil-wet.



#### Wettability of a natural rock is difficult to measure

Impossible to measure with the contact angle technique

- Roughness of the surface
- Presence of the pores

Need to rely on capillary pressure measurements (Amott and USBM index)

### Laplace law



Let us consider a spherical bubble in water with a surface tension  $\gamma$  and a radius R. The work needed for a change of radius from R to R + dR is:  $dW = -(p_{in} - p_{out}) dV + \gamma dA \Rightarrow p_{out} - p_{in} = \frac{2\gamma}{R}$ 

#### Extension of the Laplace law

For any curved interface between two fluids, the difference of pressure across the interface is expressed as:

$$p_1 - p_2 = \gamma \kappa$$
  $p_1 - p_2 = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2}\right)$ 

with  $\kappa$  the curvature of the interface or  $R_1$  and  $R_2$  the principal radii of curvature (The higher pressure is the one toward the concavity).

## Capillary rise, Jurin's law



When a capillary tube is put in water one can observe a rise of water in the capillary at a precise height

Competition between gravity and pressure forces. At the meniscus,  $P_1 = P_{atm} - \frac{2\gamma}{R}$  with R the radius of curvature.

At equilibrium we then have:  $P_{atm} = P_{atm} - \frac{2\gamma}{R} + \rho gh$ . If  $\theta$  is the contact angle,  $R = \frac{r}{\cos \theta}$ The capillary rise is then:  $h = \frac{2\gamma \cos \theta}{r\rho g}$ 

The smaller the capillary tube, the more important capillary effects are.

### Phase saturation



Ω	Total volume of the sample
$V_w$	Volume of the blue phase
V <sub>nw</sub>	Volume of the orange phase
V <sub>pores</sub>	Volume of pores (blue $+$ orange)
$\dot{\Omega} - V_{pores}$	Volume of the solid matrix

Let us consider a rigid porous solid (no deformation) filled with two phases which we will call wetting (w) and non-wetting (nw).

A fraction of the porosity is occupied by the wetting fluid while the rest is filled by the non-wetting one.

We will call saturations S the quantities  $S_w = \frac{V_w}{V_{norme}}$  and  $S_{nw} = \frac{V_{nw}}{V_{norme}}$ . We have  $S_w + S_{nw} = 1$ 

In terms of porosity,  $S_w = \frac{\phi_w}{\phi}$  and  $S_{nw} = \frac{\phi_{nw}}{\phi}$  with  $\phi_w$  and  $\phi_{nw}$  the porosity occupied respectively by the wetting and the non-wetting fluid

## Capillary pressure and phase saturations

In absence of mechanical deformation and chemical reactions, we have:  $dF = \mu_w dn_w + \mu_{nw} dn_{nw}$ 

Expressing the Helmholtz free energies of the wetting and the non-wetting fluid as  $dF_i = \mu_i dn_i - p_i dV_i$  and using the additivity of state variables  $dF = dF_{nw} + dF_w + dF^{surf}$ , we have the expression for the Helmholtz free energy stored in the pores because of capillary effects:

$$df^{surf} = -(p_{nw} - p_w) dS_w$$
 with  $df^{surf} = dF^{surf} / V_{pores}$ 

Capillary pressure is then defined as  $p_{nw} - p_w$ 

$$p_c = -rac{df^{surf}}{dS_w}$$

Capillary pressure is the intensive variable associated with the wetting fluid saturation and is then a function of  $S_w$ .

The curve  $p_c = f(S_w)$  is called Retention curve and is specific of the porous solid considered.

### Typical retention curve



The air (or non-wetting fluid) entry pressure  $p_0$  is the minimal pressure when a sample starts to desaturate

# Drainage



Drainage is the injection of non-wetting fluid in a wetting fluid saturated porous medium Imbibition is the injection of wetting-fluid in a non-wetting fluid saturated porous medium

# Capillary pressure and pore size



Infinitesimal invasion of the non-wetting fluid

$$dW = -(p_{nw} - p_w) \pi r^2 dx + (\gamma_{nw} - \gamma_w) 2\pi r dx$$
  
At equilibrium  $p_{nw} - p_w = \frac{2(\gamma_{nw} - \gamma_w)}{r} = \frac{2\gamma_{nw/w} \cos \theta}{r}$  using Young-Dupré  
The definition of capillary pressure is consistent with Laplace law

We have  $\gamma_{nw} > \gamma_w$  (with Young-Dupré)

- Capillary pressure is always positive: the wetting fluid pressure is always smaller than the non-wetting one (because of the orientation of the curvature).
- If the wetting phase is continuous the capillary pressure is homogeneous in the whole sample. If the wetting fluid saturation goes below a critical value the wetting phase becomes discontinuous and the capillary pressure becomes a local quantity depending on the meniscii  $(p_c = f(S_w))$  is no longer true.

### Retention curve and pore size

Let us consider the drainage of a porous medium by increasing steps by steps the capillary pressure (i.e. increasing the non-wetting fluid pressure).  $\Rightarrow S_w \text{ decreases and } p_c = \frac{2\gamma_{nw/w} \cos \theta}{r}.$ An increase of the capillary pressure leads to an decrease of the radius the non-wetting fluid is able to penetrate.

If we consider a bundle of capillary tubes, we can relate the capillary pressure to the transition pore:

smaller diameter  $\rightarrow$  filled with wetting-fluid

bigger diameter  $\rightarrow$  filled with non-wetting fluid



# Imbibition, drainage and hysteresis



If we try to measure the capillary curve during drainage and imbition, we observe a strong hysteresis

The modeling of pores as a bundle of capillary tubes cannot explain this hysteresis !

# Capillary hysteresis

To model the capillary hysteresis we need to consider the model of the spherical pores with cylindrical pore throats

This is called the bottleneck effect



## Mercury Intrusion Porosimetry

Mercury Intrusion Porosimetry (MIP) is a widely used technique to get the pore size distribution (PSD) of a sample



AutoPore IV Micromeritics

# Mercury Intrusion Porosimetry

### Principle

A small chunk of the sample is put inside the penetrometer. The system measures then the quantity of mercury injected at each pressure step.

Mercury is non-wetting for all materials (  $\gamma = 485 \text{ J.m}^{-2}$ ).



The derivative of the cumulative intrusion volume gives give the pore size distribution. For natural rocks there is usually one or two main peaks corresponding to the main families of pores.

Porosity and saturation change during deformation

### We have defined the saturations as $S_J = \frac{\phi_J}{\phi_0}$

Let us extend the definition to porous solids subjected to deformation (the best way to do this is to keep a Lagrangian definiton):

We can decompose the porosity after deformation as :  $\phi_J = S_J \phi_0 + \varphi_J$ The fluid saturation is then :  $S_J = \frac{\phi_J - \varphi_J}{\phi_0}$  and we still have  $\sum_J S_J = 1$  and  $\sum_J \phi_J = \phi_J$ 

The total deformation of the solid is 
$$\varphi = \phi - \phi_0 = \sum_J \varphi_J$$
  
 $d\varphi_J = \phi_0 dS_J - d\phi_J$ 

During a deformation, the porosity and the saturation of the solids change.  $\varphi_J$  represents the deformation of the volume initially occupied by the fluid *J*.



The variation of Helmholtz free energy for an unsaturated solid without deformation is:

$$df = p_w d\phi_w + p_{nw} d\phi_{nw} + \sum_i \mu_i d_i - s dT$$

Taking into account the deformation, the Helmholtz free energy of the skeleton becomes:

$$df_{sk} = \sigma d\epsilon + p_w d\phi_w + p_{nw} d\phi_{nw} + \underline{\underline{s}} : d\underline{\underline{e}} - s_{sk} dT$$

 $df_{sk} = \sigma d\epsilon + p_w d\varphi_w + p_{nw} d\varphi_{nw} + \underline{s} : d\underline{e} - s_{sk} dT - \phi_0 (p_{nw} - p_w) dS_w$ 

The skeleton is the porous solid without the *bulk* fluids. The matrix/fluid and fluid/fluid interfaces belong to the skeleton. We can then divide  $f_{sk}$  in to parts: the free energy of porous solid without interfaces, and the free energy of interfaces.

$$f_{sk} = f_{sk}^{*}\left(\epsilon, \varphi_{nw}, \varphi_{w}, \underline{\underline{e}}, S_{w}, T\right) + \phi_{0}U(S_{w})$$

We assume that U depends only on  $S_w$  and not on the deformation of the sample. It means that the interfacial energy does not affect the deformation of the sample.

#### Capillary pressure as a function of the interfacial energy

Thanks to the decomposition of  $f_{sk}$ , we have:  $\phi_0 (p_{nw} - p_w) = -\frac{\partial f_{sk}^*}{\partial S_w} - \phi_0 \frac{dU}{dS_w}$ If we consider that for infinitesimal deformation, the impact of deformation on the capillary curve is negligible, we have: :

$$p_{nw} - p_w = -\frac{dU}{dS_w}$$

We find again the expression we had derived for the capillary curve without deformation.

Using Legendre transform 
$$d\psi_{sk} = df_{sk}^* - p_{nw}d\varphi_{nw} - p_w d\varphi_w$$
  
 $d\psi_{sk} = \sigma d\epsilon - \varphi_{nw}dp_{nw} - \varphi_w dp_w + \underline{s} : d\underline{e}$   
 $\sigma = \frac{\partial \psi_{sk}}{\partial \epsilon} \qquad \phi_J = -\frac{\partial \psi_{sk}}{\partial p_J} \qquad s_{ij} = \frac{\partial \psi_{sk}}{\partial e_{ij}}$ 

Again, by identification, we obtain:

•  $\sigma = K\epsilon - b_1p_1 - b_2p_2$ 

• 
$$\varphi_1 = b_1 \epsilon + p_1 / N_{11} + p_2 / N_{12}$$

• 
$$\varphi_2 = b_2 \epsilon + p_1 / N_{12} + p_2 / N_{22}$$

• 
$$s_{ij} = 2Ge_{ij}$$

Maxwell relations giving  $N_{12} = N_{21}$ 

The stress and strain partition reads then:

$$\sigma = (1 - \phi_0) \sigma_{sk} - \phi_0 S_1 p_1 - \phi_0 S_2 p_2$$
  

$$\epsilon = (1 - \phi_0) \epsilon_{sk} + \phi_1 + \phi_2$$

If we fill the solid with only one fluid, we should retrieve the equations in the saturated case

 $\begin{array}{l} p_1 = p_2 \text{ and } \varphi_1 + \varphi_2 = \varphi \\ \Rightarrow b = b_1 + b_2 \qquad 1/N_{11} + 2/N_{12} + 1/N_{22} = 1/N \end{array}$ 

Let put the solid in a bulk of one fluid:  $\sigma = -p$  and  $p_1 = p_2 = p$ 

Similarly to what we did in the saturated case:

$$\begin{aligned} \epsilon &= \frac{\varphi_J}{\phi_0} S_J = \epsilon_{sk} = -\frac{p}{K_{sk}} \\ 1/N_{11} + 1/N_{12} &= \frac{b_1 - \phi_0 S_1}{K_{sk}} \\ 1/N_{22} + 1/N_{12} &= \frac{b_2 - \phi_0 S_2}{K_{sk}} \end{aligned}$$

### Bishop parameter

#### Let us consider two fluids in the porosity

We have  $b_1 + b_2 = b$ We can then introduce  $\chi$  such as :  $b_1 = \chi b$  and  $b_2 = b(1 - \chi)$  (1 is the wetting fluid and 2 is non-wetting)

 $\chi$  should depend on all parameters but we make the assumption that  $\chi(S_w)$ .

If we consider that the pores filled with 1 and 2 are deforming the same way (pores iso-deformation), we can write that:

$$\frac{1}{\phi_0 S_2} \frac{\partial \varphi_2}{\partial \epsilon} \Big|_{(\rho_1, \rho_2)} = \frac{1}{\phi_0 S_1} \frac{\partial \varphi_1}{\partial \epsilon} \Big|_{(\rho_1, \rho_2)}$$
$$\chi = S_1 \Rightarrow b_1 = S_1 b \text{ and } b_2 = S_2 b$$

One has to remember that it is usually not the case

### Transport in unsaturated porous media Occupation of space and wettability

#### Let us consider the case where capillary forces are dominant

The capillary number is defined as :  $Ca = \frac{v_{injected} \eta_{injected}}{\gamma_{nw/w}}$ . If Ca  $\ll$  1, capillary forces are dominant, and if  $Ca \gg 1$ , viscous forces are dominant.



#### Imbibition case

The wetting fluid is on the wall. Some globules of non-wetting fluid can be trapped when the wetting fluid snaps-off at pore throats

At the breakthrough, some oil is trapped as globules or as large patches of oil extending over several pores

### Transport in unsaturated porous media Occupation of space and wettability

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#### Drainage case

The non-wetting fluid can only penetrate the largest pores as fingers.

At the breakthrough, the wetting fluid is in the smaller pores, as a continuous film on the pore wall and as large pockets trapped between the fingers

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### Transport in unsaturated porous media Residual saturation

At some point during the injection process, only the injected fluid is produced. The displaced fluid has reached its residual saturation (in oil & gas industry it is often called irreducible saturation)

The residual saturation depends on the wettability of the medium and on the type of injection  $% \left( {{{\left[ {{{\rm{T}}_{\rm{T}}} \right]}}} \right)$ 



From Anderson 1987

### Transport in unsaturated porous media Extension of Darcy's law

Darcy's law for saturated porous media  $v = \frac{k}{n} \nabla p$ .

### Modification of Darcy's law: relative permeability

Each fluid transport can be described with an extended Darcy's law:  $kk_{*}^{w}(S_{w}) =$ 

$$v_{w} = \frac{r < w}{\eta_{w}} \nabla p_{w}$$
$$v_{nw} = \frac{kk_{r}^{nw}(S_{w})}{\eta_{nw}} \nabla p_{nw}$$

The relative permeabilities depend on the fluid saturation: the higher the fluid content, the easier the fluid can move in the porosity.  $0 < k_r^w$ ,  $k_r^{nw} < 1$ Mobility ratio :  $r = \frac{k_r^w}{k_r^{nw}} \frac{\eta_{nw}}{\eta_w}$ . If r > 1, the wetting fluid is moving more easily than the non wetting one.

Relative permeabilities are very complex quantities, depending on the wettability of the medium, the history of saturation, the connectivity of pores, the pore size distribution ...

### Transport in unsaturated porous media Relative permeabilities



Source: Stanford University

#### High wetting saturation

The mobility of the wetting fluid is higher than this of the non-wetting fluid  $\rightarrow$  wetting fluid present in the small and a part of the big pores

#### Low wetting saturation

At some point the mobility of the non-wetting fluid becomes higher than the wetting one

 $\rightarrow$  the wetting fluid moves in the small pores while the non-wetting one moves in the big pores.

### Transport in unsaturated porous media Relative permeabilities



Semi-empiric relations for relative permeabilities

#### van Genuchten/Mualem

$$k_r^w = \sqrt{S^*} \left( 1 - \left( 1 - [S^*]^{(1/m)} \right)^m \right)^2$$
  
$$S^* = \frac{S_w - S_{wr}}{1 - S_{wr}}$$

Corey

$$k_r^{nw} = (1 - S_h^2) (1 - S_h)^2$$
  
$$S_h = \frac{S_w - S_{wr}}{1 - S_{wr} - S_{nwr}}$$

Hydrodynamic regimes and residual saturations

If the capillary number increases, the capillary forces will play less and less role. The behavior of the fluids will then change from the capillary regime



DRAINAGE

Figure 9. Phase-diagram for drainage.

Hydrodynamic regimes and residual saturations

If the capillary number increases, the capillary forces will play less and less role. The behavior of the fluids will then change from the capillary regime



#### Residual saturations and hysteresis



Source : Akbarabadi & Piri 2012

#### $k_r^w$ reaches 0 at $S_w = S_{wr}$

The residual saturation is defined as the saturation at which the considered fluid stops moving in the porosity. Residual saturation depends particularly on the history of injection and on the capillary number.

Residual saturations and hysteresis



Figure 2.3: Capillary Desaturation Curve for a non wetting phase <sup>(7)</sup>

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Hysteresis of the residual saturation: resaturation and capillary trapping

### The variation of residual saturation is caused by the residual capillary trapping

### Residual trapping cannot be explained with rounded pore walls

Instead of cylindrical pore throats and spherical pores, we can used angular shapes such as triangles and cubes



Hysteresis of the residual saturation: resaturation and capillary trapping

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Instead of cylindrical pore throats and spherical pores, we can used angular shapes such as triangles and cubes



Saturated sample

Hysteresis of the residual saturation: resaturation and capillary trapping

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Instead of cylindrical pore throats and spherical pores, we can used angular shapes such as triangles and cubes



First drainage Residual water saturation

Hysteresis of the residual saturation: resaturation and capillary trapping

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Resaturation Capillary trapping of non-wetting phase

## Three-phase flow

#### Usually in oilfields, there is the superposition of oil, water and gas

Very (very) complex behavior is you want to take into account the different regimes

In the Oil & Gas engineering, the channel flow hypothesis is usually assumed

- Water is the wetting fluid and fills the small pores
- Oil is the intermediate wetting fluid and fills the intermediate pores
- Gas is the non-wetting fluid and fills the biggest pores

Transport behavior is then characterized by 3 relative permeability functions depending on the saturation of each phase  $% \left( {{{\left[ {{{\rm{T}}_{\rm{T}}} \right]}}} \right)$ 

#### There exists different formulations of these relative permeabilities

The most used is the Stone I model (1970) It assumes that the wetting (water) and the non-wetting (gas) phases are behaving as in a 2 phase flow

• 
$$k_r^{w,wog} = k_r^{w,wog}$$

• 
$$k_r^{g,wog} = k_r^{g,go}$$

• 
$$k_r^{o,wog} = f\left(k_r^{o,wo},k_r^{o,og}\right)$$

### Interfacial stress and deformation

#### In the case the interfacial forces cannot be neglected

 $U(S_w) \Rightarrow U(S_w, S_{nw}, \varphi_w, \varphi_{nw})$ Let us rewrite the free energy of the skeleton separating each fluid:

$$f_{sk} = \sigma d\epsilon + \sum_{J} p_{J} d\varphi_{J} - \phi_{0} \left( p_{nw} - p_{w} \right) dS_{w} + \underline{\underline{s}} : d\underline{\underline{s}}$$

We then have the following equations of state:

$$p_J = \frac{\partial f_{sk}}{\partial \varphi_J}$$
 and  $\phi_0 \left( p_{nw} - p_w \right) = -\frac{\partial f_{sk}}{\partial S_w}$  (same equation as previously)

Considering again the decomposition:  $f_{sk} = f_{sk}^* (\epsilon, \varphi_J, \underline{e}, S_J) + \phi_0 U(\varphi_J, S_J)$ 

$$p_J = \frac{\partial f_{sk}^*}{\partial \varphi_J} + \phi_0 \frac{\partial U}{\partial \varphi_J} \Rightarrow p_J - \phi_0 \frac{\partial U}{\partial \varphi_J} = \frac{\partial f_{sk}^*}{\partial \varphi_J}$$

We define the apparent pore pressure  $p_J^*$  as :

$$p_J^* = p_J - \phi_0 \frac{\partial U}{\partial \varphi_J}$$

### Interfacial stress and deformation

And finally :

$$d\psi_{sk} = df_{sk}^* - d\left(\sum_J p_J^* d\varphi\right) d\psi_{sk} = \sigma d\epsilon + \underline{\underline{s}} : d\underline{\underline{e}} - \sum_J \varphi_J dp_J^*$$

This is the same expression as before, but replacing  $p_J$  by  $p_J^*$ .

$$\begin{cases} \sigma = K\epsilon - bp_J^* \\ \varphi_J = b_J\epsilon + \sum_I \frac{1}{N_{I,J}} p_I^* \\ s_{ij} = 2Ge_{ij} \end{cases}$$

The apparent pore pressure is the pressure effectively transmitted by the fluid in the pore to the solid matrix taking into account the interface effects.

The expression of  $\frac{\partial U}{\partial \varphi_J}$  is usually difficult to determine and is often neglected. At 0 fluid pressure, the effect of interfacial tension can deform the sample  $\rightarrow$  prestress

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