# Mechanics and Physics of Porous Solids

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





## Introduction

- 2 Basics of thermodynamics and thermochemistry
- Basics of Mechanics
- The saturated porous solid
- 5 The unsaturated porous solid
- 6 Confined phase transitions
- Experimental considerations

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- 2 Basics of thermodynamics and thermochemistry
- Basics of Mechanics
- The saturated porous solid
- 5 The unsaturated porous solid
- 6 Confined phase transitions
  - Experimental considerations

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## 2 Basics of thermodynamics and thermochemistry

- Basics of Mechanics
- The saturated porous solid
- 5 The unsaturated porous solid
- 6 Confined phase transitions
  - Experimental considerations

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Basics of thermodynamics and thermochemistry

## Basics of Mechanics

4) The saturated porous solid

5 The unsaturated porous solid

- 6 Confined phase transitions
  - Experimental considerations

## Introduction

- 2 Basics of thermodynamics and thermochemistry
- 3 Basics of Mechanics

## The saturated porous solid

- 5) The unsaturated porous solid
- 6 Confined phase transitions
  - 7 Experimental considerations

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- 2 Basics of thermodynamics and thermochemistry
- Basics of Mechanics
- 4 The saturated porous solid
- 5 The unsaturated porous solid
- 6 Confined phase transitions
- 7 Experimental considerations

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2 Basics of thermodynamics and thermochemistry

Basics of Mechanics

The saturated porous solid

5 The unsaturated porous solid

6 Confined phase transitions

Experimental considerations

# Unconfined phase transition

Phase transition is the transformation of a substance from one phase to the other

- liquid
- gas
- solid
- supercritical



## If T and p are constant $dG \leq 0$

$$dG = \mu^J dn^J + \mu^K dn^K = \left(\mu^K - \mu^J\right) dn^{J o K} \leq 0$$

The molecules will go from the phase with the highest chemical potential to the one with the lowest until the two are equal.

# Mother and daughter phase

Phase transition consists in the transformation of one phase into the other

- The phase with the higher entropy will be called Mother Phase (1)
- The phase with the lower entropy will be called Daughter Phase (2)

The degree of supersaturation  $\Delta \mu$  is defined as:

$$\Delta \mu = \mu_2 \left( p_1, T \right) - \mu_1 \left( p_1, T \right)$$

The degree of supersaturation scales the distance from equilibrium.



The degree of supersaturation is defined for the two phases at the pressure of the mother phase even if the daughter phase has a different pressure.

- ullet if  $\Delta\mu>$  0, the mother phase is stable and the daughter phase is metastable
- $\bullet\,$  if  $\Delta\mu<$  0, the daughter phase is stable and the mother phase is metastable

If  $p_1 
eq p_2$  there can be an equilibrium even if  $\Delta \mu 
eq 0$ 

# Kelvin's law



Let us consider an water droplet is bulk air: what is the partial pressure of vapor in equilibrium with the droplet ?

At equilibrium, 
$$\mu_L^0(p_L, T) = \mu_v^0(T) + RT \ln \frac{p_v}{p_0}$$
  
 $\left(\frac{\partial \mu_L}{\partial p}\right)_{n_L,} = \left.\frac{\partial}{\partial p}\right|_{n_L,T} \left(\left.\frac{\partial G}{\partial n_L}\right)_{p,T} = \left.\frac{\partial}{\partial n_L}\right|_{p,T} \left(\left.\frac{\partial G}{\partial p}\right)_{n_L,T} = \upsilon_L(p_G, T)$   
 $\mu_L(p_L, T) = \mu_L(p_G, T) + \int_{p_G}^{p_L} \upsilon_L(p, T) dp \approx \mu_L(p_G, T) + \upsilon_L(p_L - p_G)$ 

# Kelvin's law



#### Isobaric case

In the case  $p_1 = p_2$ , we have  $\mu_L^0(p_1, T) = \mu_v^0(T) + RT \ln \frac{p_{sv}}{p_0}$ with  $p_{sv}$  the saturated vapor pressure.

Finally we obtain in the non isobaric case:

$$p_L - p_G = rac{RT}{v_L} \ln rac{p_v}{p_{sv}}$$

This equation is called *Kelvin's law*. If the pressure of the liquid phase is higher than the pressure of the gas phase, the vapor pressure will increase. We define the relative humidity  $h_R = p_v/p_{sv}$ 

# Kelvin's law and supersaturation



The mother phase is the vapor and the daughter phase is the water

The degree of supersaturation is  $\Delta \mu = \mu_L(p_1, T) - \mu_v(p_1, T) = \mu_L(p_1, T) - \mu_L(p_2, T)$ 

$$\Delta \mu = v_2(p_1 - p_2)$$
 (always valid)

In the case of evaporation :

$$\Delta \mu = -RT \ln h_R$$

for  $h_R = 99\%$ ,  $p_L - p_{atm} = -1$  kPa for  $h_R = 50\%$ ,  $p_L - p_{atm} = -100$  kPa

## Effect of solute on Kelvin's law

The presence of salt in the water changes its chemical potential

 $\mu_L(p_2, T, x) = \mu_L^0(p_1, T) + \upsilon_L(p_2 - p_1) + RT \ln(1 - x)$ Following the same procedure as before, we obtain:

$$p_L - p_G = rac{RT}{v_L} \ln rac{p_v}{p_{sv}(1-x)} = rac{RT}{v_L} \ln rac{h_R}{1-x}$$

The presence of the salt decreases the partial pressure of vapor at equilibrium. The more salt, the less the water is susceptible to evaporate.

# Evaporation and solid surface, the precondensed film

### Let us consider a vapor in contact with a solid surface

The solid is wetted by the fluid  $S = \gamma_{sv} - \gamma_{sL} - \gamma_{Lv} > 0$ The vapor is undersaturated  $\Delta \mu = \mu_L - \mu_v > 0$  (the equilibrium goes toward an evaporation)



Let us consider the existence of a film of liquid between the solid and the vapor

If the film is thin enough, a disjoining pressure is created : overlapping of the energy profiles. As a result, the energy variation for the change of thickness *e* of the film is:  $dG(e) = \mu_L dn_L + \mu_v dn_v + dW(e)$ with W(e) the interaction energy arising from the overlapping.  $W(\infty) = 0$  and W(0) = S

## Evaporation and solid surface, the precondensed film

 $dG(e) = \mu_L dn_L + \mu_v dn_v + dW(e)$ 

Considering that  $dn_L = -dn_v = de/v_L$  and using the supersaturation we obtain :

$$dG(e) = \Delta \mu \frac{de}{\nu_L} + dW(e)$$
$$\frac{dG(e)}{de} = \frac{\Delta \mu}{\nu_L} - \omega$$

 $\omega = -dW(e)/de$  is called the disjoining pressure

#### At equilibrium, dG(e)/de = 0

 $\frac{\Delta \mu}{v_L} = \omega$ . W(e) is decreasing with the thickness so the disjoining pressure is always positive. As we have considered a case where the supersaturation is positive, there exist a thickness *e* at which the system is at equilibrium. If the supersaturation were negative, the liquid film will grow infinitely.

The disjoining pressure forces the presence of a thin liquid film on the surface of the solid even if we are below the vapor saturation pressure

And finally we have at equilibrium  $p_v = \omega + p_l$ 

# Liquid solid transition

## We need to differentiate two types of liquid-solid transition

- freezing : one pure component getting solid
- crystallization : dissolved ions forming a solid

## The mother phase is the liquid and the daughter phase is the solid

For a solid, we need to replace the pressure in the expression of Gibbs free energy by the stress tensor  $\underline{\sigma}$ . A transformation on a solid will then imply two processes: deformation at constant volume, and change of volume because of increase of mole quantity.

$$\begin{aligned} dG &= \Omega dp - SdT + \mu dN & \text{for a liquid} \\ dG &= -\Omega d\sigma - \Omega_0 \underline{e} d\underline{s} - SdT + \mu dN & \text{for a solid} \end{aligned}$$

The shear defomation occurs at constant volume. If  $\underline{\sigma}$  reduces to an hydrostratic pressure, we find again the classic equation of Gibbs free enthalpy.

# Liquid solid transition : freezing

## We then have the following relations

$$\begin{split} & \left(\frac{\partial\mu}{\partial\sigma}\right)_{\underline{s},T,N} = -\left(\frac{\partial\Omega}{\partial N}\right)_{\underline{\sigma},T} = -\upsilon\left(\underline{\sigma},T\right) \\ & \left(\frac{\partial\mu}{\partial s_{ij}}\right)_{\sigma,T,N} = -\left(\frac{\partial e_{ij}\Omega_0}{\partial N}\right)_{\sigma,T} = -\upsilon\left(\underline{\sigma}_0,T\right)e_{ij} \\ & \left(\frac{\partial\mu}{\partial T}\right)_{\underline{\sigma},N} = s \end{split}$$

For a solid, shear stresses can also modify the chemical potential ! However, in the following, we will restrict ourselves only to normal stresses

# Liquid solid transition : freezing Thomson's law

Let us consider the problem of a solid subjected to an hydrostatic compressive stress

$$\mu_L(p_L, T) = \mu_0 + (p_L - p_{atm}) \upsilon_L + s_L \left(T_m^0 - T\right)$$
$$\mu_C(p_C, T) = \mu_0 + (p_C - p_{atm}) \upsilon_C + s_C \left(T_m^0 - T\right)$$

 $T_m^0$  is the melting temperature at atmospheric pressure, and  $\mu_0$  is the chemical potential of the substance at  $p_{atm}$  and  $T_m^0$ . The molar volumes are considered as independent of the temperature and the pressure.

Let  $T_m$  be the melting temperature at  $p \neq p_{atm}$ , but with both phases at the same pressure The equilibrium condition gives :

$$(p-p_{atm})\left(1-\frac{\upsilon_L}{\upsilon_C}\right) = \Delta s_m(T_m^0-T_m)$$

with  $\Delta s_m$  the melting entropy per molar volume defined as :  $\Delta s_m = \frac{s_L - s_C}{v_c}$ Increasing the pressure on the solid decreases the melting temperature if the solid is less dense than the liquid (water).

# Liquid solid transition : freezing Thomson's law

If the solid and the liquid are not at the same pressure, we obtain the following relation :

$$p_{c} - p_{atm} - (p_{L} - p_{atm}) \frac{\upsilon_{L}}{\upsilon_{C}} = \Delta s_{m} \left( T_{m}^{0} - T \right)$$
$$p_{c} - p_{L} = \Delta s_{m} \left( T_{m} - T \right)$$

where  $T_m$  is the melting temperature at  $p_c = p_L$ . If the solid has a different pressure from the liquid, then the equilibrium temperature will differ. The supersaturation is :

 $\Delta \mu = -(s_I - s_C)(T_m - T)$ 



# Crystallization from a solution

For solidification from a melt, the temperature is the source of supersaturation. In the case of a solute, it is the concentration

Let us consider the following chemical dissolution :

$$\nu_{\mathsf{s}} A_{\nu_1} B_{\nu_2} \dots \nu_{\mathsf{w}} H_2 O \Longrightarrow \nu_1 A + \nu_2 B + \dots^+ \nu_{\mathsf{w}} H_2 O$$

A, B  $\ldots$  are the chemical species composing the crystal and  $\nu$  the stoichiometric coefficients.

At equilibrium, the Gibbs free energy of reaction is equal to zero:

$$\Delta_r G = \sum_j \nu_j \mu_j = \mathbf{0} \Leftrightarrow \sum_i \nu_i \mu_i + \nu_w \mu_w = \mu_s$$

j are all the species involved, i are the ions, w the water and s the crystal.

If the crystal and the solution have the same pressure, the mass action law can be applied :  $K_s = \prod_i a_i^{\nu_i}$ 

# Crystallization from a solution

If the crystal and the solution do not have the same pressure  $\mu_s(p_s, T) = \mu_s(p_L, T) + \upsilon_s(p_s - p_l)$ 

The new equilibrium then writes :

$$\Delta_r G = 0 \Rightarrow \sum_i \nu_i \mu_i(p_L, T) + \nu_w \mu_w(p_L, T) = \mu_s(p_L, T) + \upsilon_s(p_s - p_L)$$
  
$$\Rightarrow 0 = \Delta_r G^0 - \upsilon_s(p_s - p_L) + RT \ln Q_r$$
  
$$\Rightarrow p_s - p_L = \frac{RT}{\upsilon_s} \ln S(p_L, T)$$

with  $S(p_L, T) = \frac{Q_r}{K_s}$  the ... supersaturation ... of the solution. Do not confuse the two supersaturations...

$$(\Delta \mu = \mu_s(p_L, T) - \sum_i \nu_i \mu_i(p_L, T) + \nu_w \mu_w(p_L, T) = -RT \ln S(p_L, T))$$

If a crystal is under pressure, it will be in equilibrium with a larger supersaturation. The more pressurized the crystal, the higher the solubility

# Crystallization from a solution

Creep and pressure solution

## Creep is the time-dependent permanent deformation of a sample under stress

Creep belongs to plastic deformations but occurs usually below the yield stress. In porous media creep can have different origins:

- mechanical deformation of the grains
- Closing of the fractures
- pressure solution
  - on the grain boundary, the solubility of the mineral is increased. This part dissolves compacting the grains. The dissolved mineral will then precipitate on the stress free surface decreasing further the porosity.



# Solidification and solid surface

#### What happens when a crystal come close to a solid surface ?



As for the precondensed film, there is an interaction of the two surfaces through the liquid film

We consider that the solution is oversaturated and we look at the equilibrium value of the thickness of the film.

The change of Gibbs free energy for a modification of thickness is :

$$dG(e) = \sum_{i} \mu_i(p_L, T) dn_i + \mu_w(p_L, T) dn_w + \mu_s(p_L, T) dn_s + dW(e)$$
  
$$dG(e) = \frac{de}{v_s} \left( \sum_{i} \nu_i \mu_i(p_L, T) + \nu_w \mu_w(p_L, T) - \mu_s(p_L, T) \right) + dW(e)$$

## Solidification and solid surface

As previously we obtain:

$$dG(e) = rac{de}{v_s} \Delta \mu + dW(e)$$

with  $\Delta \mu = \sum_{i} \nu_{i} \mu_{i}(p_{L}, T) + \nu_{w} \mu_{w}(p_{L}, T) - \mu_{s}(p_{L}, T)$  (ok with the definition of supersaturation)

$$rac{dG}{de} = rac{\Delta \mu}{v_s} - \omega$$

with  $\omega$  the disjoining pressure created by the interaction between the two solid surfaces. The equilibrium thickness is such as  $\omega(e) = \frac{\Delta \mu}{v_s}$ We have also  $p_s = p_l + \omega$ 

### Finally the supersaturation is $\Delta \mu = -RT \ln S$

It is negative which was the initial hypothesis (if S < 1, i.e. the crystal is not stable, then the system goes to an infinitely large film)

# Solidification and solid surface

## This can be extended to freezing

The supersaturation is  $\Delta \mu = -(s_L - s_c)(T - T_m)$ The equilibrium thickness is then :  $\omega(e) = -\Delta s_m(T - T_m)$ 

#### Premelted film

The precondensed film can be extended to the case of ice : when ice is in contact with air, a thin layer of liquid water is formed because of the disjoning pressure.

## The interaction energy can have different sources

- DLVO forces
  - Van der Waals forces
  - electostatic interaction
- non-DLVO forces
  - entropic origin : decrease of the available space for the solvent molecules when the two surfaces are brought together.

# Ice skating

## The awful truth about ice skating : you have been lied to !

Usually it is said that ice skating is made possible because the pressure created by the weight of the ice skater makes the ice melt and then lubricates the ice with a film of liquid water.

 $\rightarrow$  It is wrong !

$$(p - p_{atm})\left(1 - \frac{\upsilon_L}{\upsilon_C}\right) = \Delta s_m \left(T - T_m^0\right)$$

 $p = 70 \text{kg}/20 \text{cm} \times 2 \text{mm}, \ \Delta s_m = 1.2 \text{ MPa.K}^{-1}$  $\Rightarrow T - T_m^0 = -1.43 \text{K}$ 



The change of melting temperature is too small for polar regions, the weight of the ice skater is not enough to melt the ice if the temperature is < -1.5°C

The lubrication for ice skating comes from the premelted film created by the disjoining pressure

# Phase transition and surface energy

## At small size, the effect of surface energy is not negligible

Laplace law :  $p_G - p_L = \frac{2\gamma}{r} \Rightarrow \Delta \mu = \frac{2\gamma}{r \upsilon_L}$ The supersaturation can be created by a size effect. The curvature increases one phase pressure and shifts the equilibrium

### Ostwald ripening

If 2 bubbles a and b of different size  $(r_a > r_b)$  are present in a bulk water :

$$\Delta \mu_{a} < \Delta \mu_{b}$$

The small bubble is farther from the equilibrium than the big one  $\Rightarrow$  diffusion of the gas from the small bubble to the big one

If several sizes of crystal/bubbles/droplets...are present in a mixture, the system will evolve toward an increase of the average size

# Phase transition and surface energy Nucleation

## Example of the nucleation of a ice crystal in a bulk water

Mother phase is undersaturated :  $\Delta \mu < 0$ 

The creation of a nucleus in the bulk mother phase is a difficult process

$$\Delta G(r) = \left(\frac{4}{3}\pi r^3\right)\frac{\Delta\mu}{\upsilon_2} + 4\pi r^2\gamma_{12}$$

Competition with the gain of energy through the nucleation and the unfavorable creation of an interface between 1 and 2.

$$\Delta G(r) = \underbrace{\frac{2\pi r_c^3}{3v_2} \Delta \mu}_{\Delta G_c} \left( 2\left(\frac{r}{r_c}\right)^3 - 3\left(\frac{r}{r_c}\right)^2 \right)$$

Maximum of energy for critical size :  $r_c = -\frac{2\gamma_{12}\upsilon_2}{\Delta\mu}$ 

# Phase transition and surface energy Nucleation



### Metastability

Density fluctuations create nuclei of random sizes. If the nucleus created is smaller than the critical size it is unstable and shrinks. If it is bigger, it will grow and become more and more stable. An increase in the supersaturation (in absolute value) will lead to a decrease of the critical radius and then to an easier nucleation

# Phase transition and surface energy Nucleation



## Heterogeneous nucleation

Homogeneous nucleation (in the bulk) usually never occurs in reality. Instead nucleation occurs at specific sites on a solid surface : the presence of the surface lowers the effect of interfacial energy and then decreases the critical radius facilitating the nucleation

# Supersaturation and capillary pressure

What happens when we apply these concepts in a porous medium ?

We have defined capillary pressure as  $p_c = p_{nw} - p_w$ 

We have the supersaturation as  $\Delta \mu = \mu_2(p_1, T) - \mu_1(p_1, T) = \mu_2(p_1, T) - \mu_2(p_2, T) = \upsilon_2(p_1 - p_2)$ In an unsaturated porous media, saturation controls the difference of pressure between the present phases.

## In the case of a non-deformable porous solid

$$p_c = f(S_w) \Rightarrow \Delta \mu = f(S_w) \quad \& \quad S_w = f(p_c(h_R))$$

In particular we have the following relations :

$$\left\{ \begin{array}{ll} \Delta \mu = \upsilon_2 p_c & \text{if phase 2 is the wetting phase} \\ \Delta \mu = -\upsilon_2 p_c & \text{if phase 2 is the non wetting phase} \end{array} \right.$$

If the supersaturation is fixed ( $h_R$ , T, concentration of the solution...), then the wetting phase saturation is directly known, knowing the retention curve

## Supersaturation and pore size

## We consider that the phases are continuous

 $p_c = \frac{2\gamma_{12}\cos\theta}{R}$  with R the radius of the transition pore :  $R = \pm \frac{2\gamma_{12}\cos\theta v_2}{\Delta\mu}$ We have a direct relation between R and the supersaturation. The higher the supersaturation, the smaller the transition pore is.

For example, if we consider freezing, ice is non-wetting. As a result, it cannot penetrate the small pores. In order to force ice into the small pores, one has to increase the supersaturation i.e. decrease the temperature .

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### Equivalence between transport and phase transition

The phase transition from a wetting phase to a non-wetting phase is a drainage The phase transition from a non-wetting phase to a wetting one is an imbibition

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### The continuity of the phases is a really strong hypothesis

Let us consider a porous medium filled by one phase subjected to a phase transition to another one

The continuity of the phase implies that the nucleation rate is much smaller than the growth rate : there has to be a single nucleus growing

This is valid for freezing and drying but not for crystallization

## Poromechanics of phase transition

We will be using the exact same equations as for the unsaturated porous medium

• 
$$\sigma = K\epsilon - b_w p_w - b_{nw} p_{nw} - \alpha K(T - T_0)$$
  
•  $\varphi_w = b_w \epsilon + p_w / N_{w/w} + p_{nw} / N_{w/nw} - \alpha_{\phi_w}(T - T_0)$   
•  $\varphi_{nw} = b_{nw} \epsilon + p_w / N_{nw/w} + p_{nw} / N_{nw/nw} - \alpha_{\phi_{nw}}(T - T_0)$   
•  $s_{ij} = 2Ge_{ij}$ 

with  $\alpha$  the volumetric thermal dilation of the porous solid, and  $\alpha_{\phi_J}$  the volumetric thermal dilation of the porous space filled with the phase *J*. It can be shown that  $\alpha = \alpha_{sk}$  and that  $\alpha_{\phi_J} = \alpha_{sk}(b_J - \phi_0 S_J)$ 

#### Effectively transmitted stress

We have seen that the pressure transmitted by the phase on the porous matrix can differ from the pressure of the phase itself :  $p_j^* = p_J - \frac{\partial U}{\partial \phi_j}$ . In the case of a solid transmitted stress to the porous matrix, we have seen that  $p_s = p_L + \omega$ . This effect is symmetrical :

$$p_{C,s}^* = \omega + p_L$$
## Drying of porous medium, diffusive drying Drying and pore size distribution

Let us consider a sample filled with water and put to dry at a constant relative humidity  $h_{\!R}$ 



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# Drying of a porous medium, diffusive drying Drying regimes

## Capillary currents

We consider that the air pressure is constant. As a result, when  $S_w$  decreases,  $p_l$  decreases.

Evaporation occurs at the surface of the sample  $\rightarrow$  gradient of water saturation  $\rightarrow$  gradient of water pressure

As long as the water phase is continuous, capillary current bring water from the center of the sample to the boundaries.

These capillary currents take place as corner flows or less efficiently through the wetting film.



# Drying of a porous medium, diffusive drying Drying regimes

## Drying can be separated in two different regimes

 $1 \tau_{evap} \gg \tau_{capillary}$ 

In this regime, evaporation is slower than the redistribution of water by capillary currents. The saturation decreases homogeneously in the sample but the evaporation front does not penetrate further in the sample.

#### 2 $\tau_{capillary} \gg \tau_{evap}$

At some point of the evaporation, the capillary currents become less and less efficient as the relative permeability of water decreases. Drying is then controlled by the evaporation rate and the front penetrates further and further in the sample.

#### The behavior is then slightly different from the drainage of two immiscible fluids

Residual water is only determined by the meniscii between air and water and not by the history of drying

# Drying of porous medium, diffusive drying







Sghaier et al. 2013

## Capillary current and coffee ring effect

If the water in the sample contains ions (or particles), during the capillary regime, the capillary currents will bring these ions to the position of the evaporation front  $\Rightarrow$  accumulation and precipitation of the ions at the front : coffee ring effect

In the case of ions, efflorescence or possibility of clogging

# Drying of a porous medium, diffusive drying Drying shrinkage

We have 
$$S_L = f\left(-rac{RT}{v_L}\ln h_R
ight)$$

At the beginning of drying,  $p = p_{atm}$  and  $\sigma = -p_{atm} \Rightarrow \epsilon_0 = -\frac{p_{atm}}{K} (1-b)$ At a definite stage of drying, we have :  $\epsilon = \frac{p_{atm}}{K} (b-1) - \frac{p_c}{K} b_L$ Under the assumption of isodeformation, we have :  $\epsilon = \frac{p_{atm}}{K} (b-1) - \frac{p_c}{K} bS_L$ 

The variation of volume is then :  $\Delta \epsilon = -\frac{p_c}{K}bS_L$ 

#### The shrinkage is position dependent

 $\Delta \epsilon = f(S_L).$ 

As we have seen,  $S_L$  depends on the position if the capillary currents are not efficient enough. As a result, there is a variation of deformation between the outer part of the sample and the inner part.





## Let us consider a porous solid filled with water at a temperature $T < T_m^0$

Freezing is similar to evaporation as it is a drainage like process (ice is non-wetting) However, ice does not start at the surface but anywhere where the pore size is large enough

The nucleation rate of ice is extremely low at 'classic' temperatures : only one nuclei will be created (OK with the continuous phase hypothesis)

Considering a reference state at  $T = Tm^0$ , we have :

$$\sigma = K\epsilon - b_L p_L - b_C p_C - \alpha K \left(T - T_m^0\right)$$

At constant atmospheric pressure (i.e. at constant confining stress), we have :

$$\Delta \epsilon = \frac{b}{K} \left( S_L \left( p_L - p_{atm} \right) + S_C \left( p_C - p_{atm} \right) \right) - \alpha \left( T - T_m^0 \right)$$
$$\Delta \epsilon = \frac{b}{K} \left( \left( p_L - p_{atm} \right) + \left( 1 - S_L \right) p_{cap} \right) - \alpha \left( T - T_m^0 \right)$$

Closing the system of equations

$$\Delta \epsilon = rac{b}{\mathcal{K}} \left( S_L \left( p_L - p_{atm} 
ight) + S_C \left( p_C - p_{atm} 
ight) 
ight) - lpha \left( \mathcal{T} - \mathcal{T}_m^0 
ight)$$

The first term corresponds to hydraulic pressure, the second to *cryogenic swelling* and the third to thermal expansion

If we know the retention curve, Thomson's equation and boundary conditions, we can calculate the whole behavior.

$$p_{cap} + (p_L - p_{atm}) \left(1 - \frac{v_L}{v_C}\right) = \Delta s_m \left(T_m^0 - T\right)$$

#### Hydraulic pressure in the undrained case

The calculation of the conservation of the mole quantity in the medium leads to the following equation (see derivation in O. Coussy's book) :

$$p_L = S_C \left( 1 - \frac{v_L^0}{v_C^0} \right) \frac{K_L K_C}{S_L K_L + S_C K_C}$$

Interestingly, we find that injecting this equation in Thomson equation, we obtain  $p_C \approx p_L$ . Using this in the deformation equation and neglecting the effect of the temperature expansion, we obtain :

$$\epsilon = \frac{bp_L}{K}$$

In the undrained case, expansion is mainly produced by the change of volume upon freezing.

## Freezing Cryosuction



Let us consider the transient evolution when the temperature decreases

1 The system is at equilibrium at a temperature following Thomson's law :  $T_1 = T_m + rac{2\gamma}{r_1 \Delta s_m}$ 

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- 2 We decrease the temperature to a new temperature such as  $T_2 = T_m + rac{2\gamma}{r_2\Delta s_m}$
- 3 The system starts freezing until it reaches the new pore throat. As  $T_2 < T_1$ ,  $p_c p_L$  increases. In an ideal drained case,  $p_L$  is constant and the increase in capillary pressure is made by the increase of ice pressure.

If we are not in an ideal drained case, the decrease of liquid pressure creates a gradient which triggers movement of water from the small pores to the frozen pore (through the wetting film) : this is cryogenic swelling. This movement of water stops when the equilibrium is reached and all the water has reached pressure  $p_L$ , determined by Thomson's equation.



Because of cryosuction, a sample swells a little even if the change of volume from liquid to solid is negative

Hydraulic pressure is created for a undrained freezing, forming ice decreases the volume available for liquid water and then increases its pressure (9 % density change)

Powers (1900-1997) discovered that adding air voids in concrete helps to decrease this hydraulic pressure acting as a buffer. Different theories are used to determine the optimal spacing and the size of these air voids (numerous enough to absorb the hydraulic pressure, but not too many as to decrease the mechanical strength)





# Crystallization pressure and salt weathering

#### There are 2 fundamental difference between salt weathering and freezing

- With freezing, the supersaturation  $\Delta \mu$  is never high enough to allow multiple nucleation. With salt crystallization, depending on the supersaturation process (temperature or evaporation), the supersaturation can be high enough to nucleate in numerous positions.
- In freezing, capillary currents do not impact the localization of the solidification. For salt weathering, as solute is transported by water, capillary currents impact strongly the localization.

## Correns and Steinborn pioneer experiment 1939 and 1949



Correns measured the pressure needed to stop the growth of the potassium alum crystal from the supersaturated solution

He postulated that the same phenomenon is applicable to porous media : the crystal growth toward the pore wall and then applies a pressure on it which is the cause of the damages observed

Let us consider a crystal growing in a pore



## At first the crystal is out of interaction from the pore wall

Considering the curvature of the crystal we have :  $\frac{2\gamma}{r} = \frac{RT}{v_s} \ln S$ There is no crystallization pressure because the crystal is too far from the pore wall

#### Let us consider a crystal growing in a pore



#### As the crystal keeps growing, it finally reaches the interaction range of the pore wall

Creation of the disjoining pressure through the remaining film of solution, considering the mechanical equilibrium of the crystal we then have :

$$p_s - (p_l + \omega) = rac{2\gamma}{r_p - \delta} \Rightarrow \omega = rac{RT}{\upsilon_s} \ln S - rac{2\gamma}{r_p - \delta}$$

The crystallization pressure transmitted by the crystal to the pore is then the disjoining pressure created when the crystal comes close to the pore wall. It corresponds to the difference between the driving force of crystallization  $\left(\frac{RT}{v_{s}} \ln S\right)$  and the curvature the crystal is forced to have  $\left(\frac{2\gamma}{r_{p}-\delta}\right)$ 

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# Why crystallization pressure is still an issue after 100 years of research

Almost 100 years after Correns and Steinborn experiment, crystallization pressure is not unanimously adopted

- VER modelization of crystallization pressure is particulary difficult
  - the crystal phase is NOT continuous. Contrary to ice, nucleation rate is high
  - shape of real crystals is not rounded but with flat/terrace surfaces (Wulff shape)
  - crystallization pressure is time and space dependent : modelization of capillary currents, nucleation rate, growth rate, pore space . . . necessary to have a comprehensive understanding of crystallization pressure
- No experimental proof of the thermodynamical interpretation of crystallization pressure
  - experiments in natural rock cores : no direct observation
  - the film between crystal and matrix has never been observed
  - a lot of salts do not create crystallization pressure
  - no reproducible results on crystallization damages

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## Still a hot topic of research !

You guessed right, it is going to be the topic of the exam !

Cement is ever present in human activities and is the most produced porous medium In 2010, 3.3 billions of tons were produced, 250 billions \$ in 2013 revenues. More than 50% is product by China

## Even if cement is known since the Romans, it is still a hot topic of research

- high performance cements
- durability of cements
- difficult environmental conditions
- limiting the cement industry footprint

#### Cement, mortar and (reinforced) concrete

- $\bullet~{\rm Cement} \to {\rm basic}$  product. Composed of grains of the reactive material (mainly  ${\rm CaO}$  and silicates)
- $\bullet\,$  Mortar  $\to$  Cement with added sand. Increase the mechanical properties of the cement paste and decreases the cost
- Concrete  $\rightarrow$  Mortar with aggregate (gravel)
- $\bullet$  Reinforced concrete  $\to$  Steel bars are added to the final product : increases the tensile resistance

### Brief history

- Cement products are known since the Romans
- First real cement description XIXth century, Louis Vicat, and then the pattern of Joseph Aspdin 1824 (Portland cement)
- Reinforced concrete (J. Monier) and in 1889 first bridge in reinforced concrete
- Hoover Dam 1936

#### Production of cement

Cement is produced in 3 main steps.

• Quarry of the raw material : 80% of limestone (providing the lime) and 20% of clay (providing the metallic elements and Si).

Main constituents are then :

- CaO (C in the cement notation)
- SiO<sub>2</sub> (S)
- Al<sub>2</sub>Õ<sub>3</sub> (A)
- Fe<sub>2</sub>O<sub>3</sub> (F)
- Combustion of the raw materials at high temperature (1450°C ). Decarbonation of the calcite  $(CaCO_3=CaO+CO_2)$ .
  - the final product is called Clinker and is made of 4 main different main phases
    - C<sub>3</sub>S Alite
    - C<sub>2</sub>S Belite
    - C<sub>3</sub>A
    - C<sub>4</sub>AF
- Grinding : the clinker is ground to increase the specific surface area and then control the speed of reaction
  - $\approx 320 380 \text{ m}^2/\text{kg}$  for multipurpose cements
  - $\bullet~\approx 450-650~m^2/kg$  for rapid hardening cements
  - $\bullet\,$  usually 15 % in mass below 5  $\mu m$  and 5 % in mass above 45  $\mu m$  particles

#### A cement hardens (or sets) but does not dry !

In order to get a solid from the cement powder, one has to add some water. The stoichiometry is around water/cement = 0.42 (in mass). Usually, for practical reasons, higher ratios are used (typically 0.6). The reaction of the cement powder with water is called hydration. The reaction lasts several hours to be complete.

#### Main reactions

 $C_2S + H = C - S - H + CH$  $C_3S + H = C - S - H + CH$ 

- C-S-H are the main constituent of the solid cement (50% ), and are responsible of the mechanical properties. Their composition is actually extremely complex and are the reason why the chemistry of the cement is still not fully comprehended.
- CH is called portlandite. It is soluble in water and buffers the in-pore solution at pH = 12.4.

#### Formation of the solid matrix

The surface of the grains in contact with water start to react. The CSH are formed on the nucleation sites of the grains and create a percolating cluster between all grains (gel). This skeleton densifies following the evolution of the reaction and hardens

Time		
Pore kind	Pore size range	Origin
Large voids	0.1 - 1 mm	Air bubble during mixing
Capillary pore	(1) 50nm - 10 $\mu$ m	Excess water
	(2) 10 - 50 nm	
Open gel	1 - 10 nm	CSH "low density"
Dense gel	1.2 nm	CSH high density
Mono-layer	< 0.5 nm	pores inside the grains

How to improve concrete ?

## Mechanical properties

Concrete is characterized by a high compressive strength but a low tensile strength  $\rightarrow$  reinforced concrete with steel bars

During its life, concrete is subjected to a lot a external interactions which decrease its mechanical resistance

- Physical actions
  - Freezing/thawing
  - Water content change
  - Temperature stress
- Chemical actions
  - Carbonation
  - Alkali silica reaction
  - Sulfate attack
  - Steel corrosion

• . .

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- Hydraulic pressure
  - undrained case
  - drained case but with low permeability
- Cryogenic swelling

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 $\rightarrow$  Shrinkage/expansion linked to the evolution of water saturation

$$\epsilon = -\frac{p_c}{K}bS_L$$

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Shrinkage expansion linked to the evolution of temperature  $\epsilon \propto \alpha T$ 

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atmospheric  $CO_2$  + water  $\Rightarrow$  decrease pH Dissolution of portlandite and precipitation of calcite Decrease of the mechanical properties

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Reaction between  $OH^-$  in the pore solution and the silica of the aggregates

Creation of a swelling gel between the cement paste and the aggregates (several similar reactions depending on the minerals present)

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Presence of sulfate ions (external or internal)

Group of reaction involving sulfate ions and responsible of loss of cohesion in the paste and cracks

 $\rightarrow$
## Some notions on cement and concrete

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pH of in pore solution : 12.4  $\Rightarrow$  passivation of the armature

→ Decrease of pH because of CO2, depassivation and corrosion.

# Contents

## Introduction

2 Basics of thermodynamics and thermochemistry

Basics of Mechanics

The saturated porous solid

5 The unsaturated porous solid

- 6 Confined phase transitions
- Experimental considerations