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Evaporation/condensation of water in a granular medium, restricted to the pendular regime: the EWGM model

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In this draft document, comments are written *like this*.

Preamble

A new model for evaporation/condensation in wet granular media has been sketched in the thesis of Salwa (MANSOUR, 2015) [Chapt. 6, sect. 2]. The ideas of this continuous model are taken up here and completed by detailed equations. In particular, the assumptions are listed in an exhaustive way and a discussion is conducted to identify the validity of the model, called EWGM, which stands for “Evaporation in Wet Granular Media”.

There is a strong link also with the preliminary work of DELANNAY and MCNAMARA (2015).

Abstract

to be written...

1 Introduction

In the framework of ARPHYMAT project, many experiments were performed using dry sand. In fact, due to the humidity of the experiment room (where the humidity in Brittany is often important, even in summer days), we suspect that the sand didn’t stay totally dry and that a small quantity of liquid water existed between the sand grains under the form of bridges, *i.e.* the wet porous medium was in pendular regime. To model the phase change phenomenon, which comes from the evaporation of liquid water (pendular regime) present in the granular porous medium, an appropriate physical model must be used.

In literature, a great number of different physical models have been presented to deal with heat and mass transfer in an unsaturated porous medium. Let’s cite, *e.g.* , HADLEY (1985); MOYNE and DEGIOVANNI (1985); ZHANG and DATTA (2004); OUSEGUI *et al.* (2010)...

Among them, UDELL (1985) presented a study of heat and mass transfer in a porous medium saturated with liquid and vapor phases of a single component fluid. Gravity, capillarity, multiphase flow and phase change effects was included. In a more recent study, BRIDGE *et al.* (2003) have presented an extension of what was proposed by UDELL (1985) by adding the energy equation to the system. In these two studies the authors were interested in the steady state case.

Another interesting study is that presented by [DAYAN and GLUEKLER \(1982\)](#) where a model for transient heat and mass transfer has been developed for a porous medium containing water (funicular regime), vapor and air. Their physical model is divided into two zones: dry and wet. A similar study is that of [MIN and EMMONS \(1972\)](#) who studied the transient drying of a porous medium in pendular regime where two mechanisms of mass transfer were considered: the pressure driven convective flow governed by Darcy's law and the molecular diffusion of the gaseous components.

Ici, il faudrait citer le travail de [DELANNAY and MCNAMARA \(2015\)](#)...

In all previous studies, the effective thermal conductivity λ_e was taken as a constant. However, many works ([BRANDON and MITCHELL, 1989](#); [TARNAWSKI and LEONG, 2000](#); [GÉMINARD and GAYVALLET, 2001](#); [LU et al., 2007](#); [CHEN, 2008](#); [SMITS et al., 2010](#); [DONG et al., 2015](#)) mentioned that the presence of liquid water can increase substantially the value of thermal conductivity (liquid water has a thermal conductivity much higher than that of air). For this reason, we present here a physical model that describes heat and mass transfer in a wet porous medium with λ_e dependent on water content.

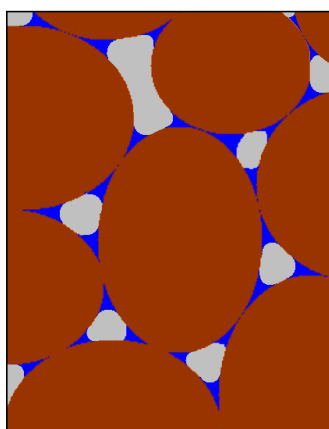


Figure 1: Pendular regime – when a small quantity of liquid water (blue) is contained inside a granular medium, it is located around the contacts between the grains (brown), as bridges which favor the heat flux. Gas is drawn in light gray.

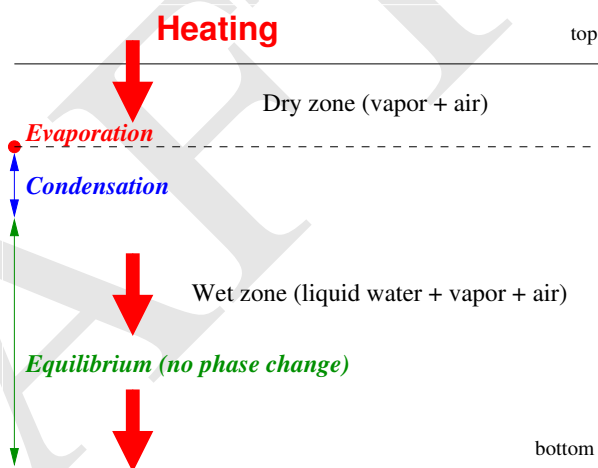


Figure 2: A diagram representing the expected results of the phase change problem showing the existence of an evaporation and condensation zones in the wet zone.

In our model, the quantity of liquid water is small and located around the contact points of the wet zone (see Figure 1): this is called the pendular regime. The liquid fraction is an unknown and may vary from place to place. Liquid water is assumed immobile at pore scale because it is blocked by the capillary forces at the grains' surface whereas water can move at domain scale only under its vapor phase, by diffusion through air. Other assumptions are listed in next section. The value of λ_e is calculated from a separated model at microscale, assuming the static mechanical equilibrium for a meniscus; as a result, λ_e , which theoretically depends only on the location of the liquid water, may experience a hysteretic behavior due to the complex appearance/disappearance of the liquid menisci.

Figure 2 describe a situation where a wet porous medium is heating at its top boundary, and shows the presence of both a thin zone of evaporation above a thin zone of condensation. These two simultaneous processes have been mentioned by [MIN and EMMONS \(1972\)](#), [UDELL \(1985\)](#), [ROTH \(2012\)](#) and other authors. During the evaporation, some quantity of liquid near the dry-wet limit is changed into gas, trying to increase its volume; this induces a local increase of pressure and the gas created flows towards

low pressure regions, *i.e.* in both upward and downward directions. When reaching a colder region, this warm gas recondensate on the liquid menisci. We think that our model is rich enough to reproduce the above-mentioned simultaneous evaporation/condensation.

Ajouter que ce phénomène d'évaporation/recondensation est consistant avec la migration de la vapeur d'eau vers les zones froides – Beaucoup d'études ont été consacrées à cette migration sous l'effet d'un gradient thermique, à la fois par des modèles (PHILIP and DE VRIES, 1957; DE VRIES, 1958; HUANG, 1979; OUSEGUI et al., 2010) et des expériences (THORVALDSSON and SKJÖLDEBRAND, 1998). On doit cependant préciser que certains de ces modèles éliminent les termes non-linéaires : on s'attend alors à un comportement très lissé des variables ; assez curieusement HUANG (1979) propose un système d'équation très similaire au mien, avec des termes non-linéaires (tous ?) mais n'obtient pas de front raide pour la fraction liquide...

Attention, la zone d'équilibre, précisée de couleur verte sur la Fig. 2, ne peut être possible que parce que le gradient est très faible dans la partie basse du domaine...

Ici, il faudrait enfin citer l'article de SMITS et al. (2011) ! Il semble utiliser une approche hors équilibre...

à citer pour les équations en multicomposants multiphasiques : MARCHAND et al. (2013); LIZAIK (2008)

2 Physical description of the EWGM model

2.1 Scales

The following scaled must be distinguished:

- (i) The *microscale*, or pore scale, is the smaller one.
- (ii) The *mesoscale* is bigger, since it covers many grains; however physical properties at this scale are still uniform in space; therefore useful properties are well defined at this scale.
- (iii) The *macroscale* (problem scale, or domain scale) is the largest one: equations of the problem are written at this level.

2.2 Hypothesis

- H₁. The porous medium is constituted by solid, impermeable spheres of same radius R_0 , packing in a random way but with a known statistical gap distribution.
- H₂. There is only a small quantity of liquid water in the porous medium (pendular regime).
- H₃. The permeability of the porous medium is not affected by the presence of liquid water.
- H₄. The liquid water doesn't move at the microscale.
- H₅. Air and water vapor diffuse through each other due to the concentration gradients, and the gas (as a whole) moves under pressure gradients.
- H₆. Gravity is neglected (gravity forces are small compared to the capillary ones). *(cependant, cela pourrait être remis en cause pour les plus gros ménisques – pour certains milieux granulaires, il y a des grands gaps; et aussi à la rupture d'un ménisque d'axe horizontal, l'eau liquide restante a tendance à descendre après sa rupture entre deux grains éloignés)*
- H₇. Porosity is constant at mesoscale.

- H₈. Thermodynamic equilibrium is assumed between the three phases (*i. e.* , at the same location, solid matrix, liquid water and its vapor are at the same temperature) at both microscale and mesoscale. *(not sure... due to the upscaling, mesoscale only is perhaps sufficient?)*
- H₉. Diffusion equilibrium is assumed through the gas (*i. e.* , at the same location, water vapor doesn't diffuse through the air – it means that water vapor has the same value against an interface and away from it) at both microscale and mesoscale. *(not sure... due to the upscaling, mesoscale only is perhaps sufficient?)*
- H₁₀. Diffusion equilibrium at the interface: the partial pressure of water vapor at the interface is always equal to the saturation pressure. *(Cela exclut un flux évaporatif fournit par l'équation de Hertz-Knudsen, provenant de la dynamique moléculaire (AJAEV, 2012), p. 149)*
- H₁₁. Gaseous components (water vapor, air) obey the ideal gas law.

2.3 Main unknowns

- U₁. The temperature T (unique, due to H₈).
- U₂. The pressure p_g of the gas.
- U₃. The density ρ_g of the gas.
- U₄. The velocity of the gas \mathbf{v}_g .
- U₅. The liquid fraction α_l (ratio of the liquid volume to the void volume – also called degree of saturation).
- U₆. The partial pressure of water vapor p_w .
- U₇. The density of water vapor ρ_w .
- U₈. The total curvature of the liquid menisci κ (constant over the whole surface of each meniscus).

Auxiliary unknowns, as the air density ρ_a , the partial pressure of air p_a , or the effective thermal conductivity λ_e , will be expressed in terms of the main unknowns.

All the unknown variables depend on both the space position \mathbf{x} and the time t .

2.4 Equations

Most important equations consist of balance equations for the mass of each component (water and air), and that concerning the energy. Others are interface equations, state or phenomenological laws.

In order to close the problem and according to the number of unknowns previously listed, we need 8 equations. We choose:

- E₁. Mass conservation of water.
- E₂. Mass conservation of air.
- E₃. Energy conservation.
- E₄. The ideal gas law for the water vapor.
- E₅. The ideal gas law for the binary mixture.
- E₆. Darcy law.

E₇. Liquid/vapor equilibrium at interfaces (Kelvin law).

E₈. A relation between the liquid fraction and the curvature of the liquid menisci.

These equations, all valid at macroscale, are detailed below.

Mass conservation of water

$$\frac{\partial}{\partial t} [\alpha_l \phi \rho_l + (1 - \alpha_l) \phi \rho_w] + \text{div}(\rho_w \mathbf{v}_w) = 0 \quad (1)$$

The term $\alpha_l \phi \rho_l$ corresponds to the mass of the liquid water in a unit control volume, whereas $(1 - \alpha_l) \phi \rho_w$ is the mass of the water vapor.

$\rho_w \mathbf{v}_w$ is the mass flux of the water (vapor only, because the liquid phase is immobile). Note that \mathbf{v}_w is not the interstitial velocity (*i. e.* the real mean velocity in the pores) but the effective velocity (known also as the Darcy velocity) that makes sense at mesoscale; this will be the case for all other velocities encountered in this document.

ϕ is the porosity of the medium, α_l is the fraction of the void occupied by the liquid water. Both quantities lie in the interval $[0, 1]$.

The variables ρ_w and \mathbf{v}_w depend on both \mathbf{x} and t . ρ_l and ϕ are supposed to be constant.

Since one new variable is introduced here (\mathbf{v}_w), we have to specify one new relation, which is the Fick law (phenomenological law), written below.

Mass conservation of air

$$\frac{\partial}{\partial t} [(1 - \alpha_l) \phi \rho_a] + \text{div}(\rho_a \mathbf{v}_a) = 0$$

The term $(1 - \alpha_l) \phi \rho_a$ is the mass of the air in a unit control volume. $\rho_a \mathbf{v}_a$ is the mass flux of the air.

As for the water, the variables ρ_a and \mathbf{v}_a depend on both \mathbf{x} and t .

The mass balance for the whole fluid can be obtained by summing the two previous equations; it writes:

$$\frac{\partial}{\partial t} [\alpha_l \phi \rho_l + (1 - \alpha_l) \phi \rho_g] + \text{div}(\rho_g \mathbf{v}_g) = 0 \quad (2)$$

ρ_g is the density of the gas, and \mathbf{v}_g is the velocity of the gas. This latter equation is more convenient to express the Darcy law (which corresponds to the momentum balance for the gas inside the porous medium), because it uses the barycentric average velocity of the two components:

$$\rho_g \mathbf{v}_g = \rho_a \mathbf{v}_a + \rho_w \mathbf{v}_w$$

Energy conservation

Internal energy E_i (no mechanical energy!) can be decomposed as:

- the solid part, $(1 - \phi) \rho_s C_s T$
- the liquid part, $\alpha_l \phi \rho_l C_l T$
- the gas binary mixture part, $(1 - \alpha_l) \phi \rho_g C_{v,g} T$

Be aware that the transport term concerns only the gas part, because the liquid doesn't move. Therefore the energy conservation writes:

$$\frac{\partial}{\partial t}(E_i) + \text{div}[(1 - \alpha_l)\phi \rho_g C_{p,g} T \mathbf{v}_g] = \text{div}(\lambda_e \nabla T) + \rho_l \frac{\partial \alpha_l}{\partial t} \phi L \quad (3)$$

E_i is the effective internal energy for the whole medium, whereas $C_{p,g}$ and $C_{v,g}$ are the mass specific heats of the gas. Moreover, we have:

$$C_{v,g} = \omega_w C_{v,w} + (1 - \omega_w) C_{v,a}$$

and

$$C_{p,g} = C_{v,g} + \frac{R}{M_g}$$

where $\omega_w = \rho_w / \rho_g$ is the mass fraction of vapor. C_l (resp. C_s , $C_{p,w}$, $C_{p,a}$) is the mass specific heat of liquid water (resp. of solid, water vapor and air). M_g is the molar mass of the gas, detailed below.

There is only one temperature T , because thermal equilibrium is assumed between the three phases (as specified by hypothesis H₇).

The second term in the right-hand-side of the same equation, $\rho_l \frac{\partial \alpha_l}{\partial t} \phi L$, is the latent heat released (resp. absorbed) during the condensation (resp. evaporation) of water vapor when the liquid volume increases (resp. decreases).

Notice that the heat source coming from the dissipation of the viscous forces is neglected.

Ideal gas for the water vapor

$$\frac{p_w}{\rho_w} = \frac{R}{M_w} T \quad (4)$$

R is the ideal gas law constant and M_w is the molar mass of the water vapor.

Ideal gas law for the binary mixture

$$\frac{p_g}{\rho_g} = \frac{R}{M_g} T$$

The molar mass of the mixture M_g depends on the percentage of the components; it can be calculated in many ways (see *e. g.* [BALMER \(2011\)](#)) and one of them uses the mass fraction of each component:

$$\frac{1}{M_g} = \frac{\rho_w}{\rho_g} \frac{1}{M_w} + \frac{\rho_a}{\rho_g} \frac{1}{M_a} = \frac{\rho_w}{\rho_g} \left(\frac{1}{M_w} - \frac{1}{M_a} \right) + \frac{1}{M_a}$$

So, the new state equation for the gas mixture is (using $\rho_w + \rho_a = \rho_g$):

$$\frac{p_g}{\rho_g} = RT \left[\frac{\rho_w}{\rho_g} \left(\frac{1}{M_w} - \frac{1}{M_a} \right) + \frac{1}{M_a} \right] \quad (5)$$

Darcy law

$$\mathbf{v}_g = -\frac{K_g}{\mu_g} \nabla p_g \quad (6)$$

As mentioned above, the Darcy law corresponds to the momentum balance of the gas flowing through the porous medium (this balance is reduced to viscous dissipation: inertia terms are neglected because velocity of the gas is supposed to be very small). It requires of \mathbf{v}_g to be the barycentric average

velocity.

K_g is the permeability of the porous matrix (for the gas flow). It depends not only on the value of the porosity but also on the tortuosity of the medium. When liquid fraction is not small, the permeability cannot be supposed constant, because the porosity for the gas reduces. We take the following Kozeny-Carman law (COSTA, 2006):

$$K_g = C_{kc} \frac{\phi_0^3}{(1 - \phi_0)^2}$$

where ϕ_0 is the porosity of the porous material. In our case, we have to replaced it by $(1 - \alpha_l) \phi$, due to the presence of the liquid water. Therefore:

$$K_g = C_{kc} \frac{(1 - \alpha_l)^3 \phi^3}{[1 - (1 - \alpha_l) \phi]^2}$$

μ_g is the dynamic viscosity of the gas. *(en toute rigueur, la viscosité du gaz μ_g dépend des autres variables, et donc de la position x et du temps t mais, par simplification, on prendra μ_g constant)*

Equilibrium or non-equilibrium at the pore scale?

First of all, the liquid/vapor equilibrium at interface obeys the Kelvin law:

$$RH = \frac{p_{w,I}}{p_{w,sat}(T)} = \exp\left(\frac{Vm_l \kappa \sigma(T)}{RT}\right) = F_1(T, \kappa) \quad (7)$$

RH is the relative humidity close to the liquid/gas interface. κ is the total curvature of the interface (by convention here, $\kappa < 0$ for a concave meniscus, and $\kappa > 0$ for a convex one like a droplet), σ is the surface tension of water in presence of air, and Vm_l is the molar volume of liquid water. $p_{w,I}$ is the partial pressure of vapor against the liquid interface. It is equal to the vapor pressure at saturation only for flat interfaces ($\kappa = 0$).

For **slow transfers**, we may suppose that both temperature and vapor concentration are uniform at the pore scale. In this case, the equilibrium condition writes:

$$p_w = p_{w,I} \quad (8)$$

everywhere around a given liquid meniscus. Therefore, the general condition for p_w leads to a twofold equation, according the presence of liquid water (*i. e.*, whether the porous medium is locally wet or dry):

$$\begin{cases} \text{if } \alpha_l > 0 & \text{then } p_w = F_1(T, \kappa) p_{w,sat}(T) \\ \text{otherwise, if } \alpha_l = 0 & \text{then } p_w < F_1(T, \kappa) p_{w,sat}(T) \end{cases} \quad (9)$$

For consistency, the F_1 function in (9b) must be taken at $\alpha_l = 0$. *(dans le cas d'un modèle toroïdal, on a $\kappa \rightarrow -\infty$ quand $\alpha_l \rightarrow 0$, ce qui revient à écrire $p_w < 0$, mais cette contradiction n'est qu'apparente car dans un tel modèle, la fraction liquide n'est jamais nulle. Il reste toutefois une singularité possible au voisinage de $p_w = 0$)*

In the case of **non-slow transfers**, a shift must be introduced between $p_{w,I}$ (always equal to the value at saturation) and the vapor pressure inside the pore; see for example OUSEGUI et al. (2010), eq. (29), where the authors apply a non-equilibrium vapor pressure model for bread baking.

$$p_w - p_{w,I} = F_2\left(\alpha_l, \frac{\partial \alpha_l}{\partial t}\right) \quad (10)$$

The exact meaning of function F_2 is not given here; the detailed derivation of the previous equation will be explained in an other document *(or in a future appendix)*. Let's just specify that it comes from the

Fick law applied to a 1-D small gas volume representing the pore, and that it includes both the surface area of the liquid meniscus and the number of menisci per unit volume. *(l'équation 10 est analogue à celle numérotée (11) dans DELANNAY and MCNAMARA (2015))*

The general condition writes therefore in a slightly different form than the previous one:

$$\left\{ \begin{array}{ll} \text{if } \alpha_l > 0 & \text{then } p_w = F_1(T, \kappa) p_{w,\text{sat}}(T) + F_2 \left(\alpha_l, \frac{\partial \alpha_l}{\partial t} \right) \\ \text{otherwise, if } \alpha_l = 0 & \text{then } p_w < F_1(T, \kappa) p_{w,\text{sat}}(T) + F_2 \left(\alpha_l, \frac{\partial \alpha_l}{\partial t} \right) \end{array} \right. \quad (11)$$

(revoir Zhang & Datta, 2004, cités d'ailleurs par Ousegui et al., 2010, qui évoquent des problèmes mathématiques si on suppose l'équilibre de la concentration de vapeur d'eau – peut-être ce problème disparaît-il dans notre cas, à cause de l'introduction explicite de la relation 12)

Another idea is to use, or try to use, the results of SHAHRAEENI and OR (2010) concerning the dynamics the evaporation/condensation at the pore scale. From their results, it is worth noting that the typical time scales involved in capillary condensation range in a very large interval (from microseconds to hours, depending of the ambient relative humidity); this latter fact should rise some difficulties in modeling this phenomenon.

The curvature κ depends on both \mathbf{x} and t . Vm_l is of course a physical constant but surface tension σ varies with temperature. For temperature not greater than 100 C, we can use the empirical law:

$$\sigma(T) \approx 76 \times 10^{-3} - 0.17 \times 10^{-3} T$$

where T must be expressed in Celsius. Other approximations covering the whole temperature interval (up to the critical temperature of water) are also possible (KAVIANY, 1999; VARGAFTIK et al., 1983); it will be described in another document, describing the numerical implementation. The surface tension doesn't depend the curvature of the liquid-gas interface (HAYE and BRUIN (1994) made some investigations using molecular dynamics but found that the curvature influence is negligible).

Note that for a flat interface ($\kappa = 0$), we find the classical interface condition:

$$p_w = p_{w,\text{sat}}(T)$$

Note also that the use of the law $p_{w,\text{sat}}$ implicitly defines the temperature of vaporization for the water (actually $T_{w,\text{sat}}(p)$ is the inverse relation). For the water, many practical approximations exist; for low temperatures, the Rankine formula, valid for temperature ranged from 5 C to 140 C, is:

$$p_{w,\text{sat}}(T) = \exp \left(13.7 - \frac{5120}{T} \right)$$

(T in Kelvin, P in atmosphere).

For higher temperatures, the following Duperray relation is valid for temperature ranged from 90 C to 300 C:

$$p_{w,\text{sat}}(T) = \left(\frac{T}{100} \right)^4$$

(T in Celsius, P in atmosphere).

(La présence des interfaces liquides n'est liée qu'à la valeur de la fraction liquide α_l . Voir cependant la limitation L-b ci-dessous qui semble indiquer que les plus petits ménisques risquent de ne pas exister à cause de la dépression interne)

Relation between the liquid fraction and the curvature of the liquid menisci

The 8th and last equation is not always easy to write under a compact, close form. It comes from a model describing (under some assumptions) the shape of the liquid menisci, thus allowing to derive a local relation between the volume of a liquid meniscus (which is closely related to the liquid fraction) and the total curvature of its interface. For the moment, we will write this last equation under a generic form:

$$F_3(\alpha_l, \kappa) = 0 \quad (12)$$

Few models are outlined below:

- the simplest model is that used by [MIN and EMMONS \(1972\)](#); it assumes implicitly that the interface of the menisci is always flat (see figure 3), since the Clausius-Clapeyron equation for water is used in their work to specify the saturation vapor pressure. However, it doesn't make any assumption for the shape of the grains. Due to the flat interfaces, the total curvature κ is always zero, whatever the liquid fraction is, and this is represented in figure 4. Since we are in the pendular regime, only small values of α_l are valid; we arbitrarily impose $\alpha_l < 0.2$. In this case, equation 12 obviously becomes:

$$\kappa = 0$$

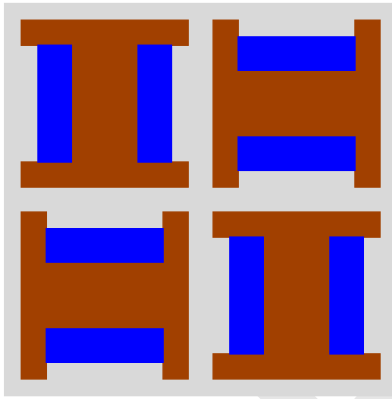


Figure 3: Simplest model for the liquid menisci (schematic view at pore scale – solid in brown, liquid in blue, gas in light gray): it doesn't make any assumption for the shape of the grains, but the liquid interfaces are all flat.

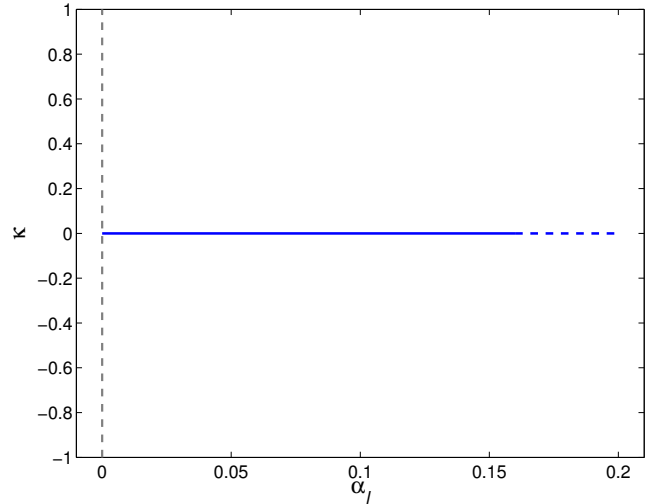


Figure 4: Liquid fraction / curvature relation, corresponding to figure 3: total curvature is always zero, whatever the liquid volume is. In the pendular regime, the liquid fraction α_l is supposed to remain small.

- the classical toroidal meniscus model. While many authors worked with the toroidal approximation (([KRALCHEVSKY and NAGAYAMA, 2001](#), Chapt. 11), [MEGIAS-ALGUACIL and GAUCKLER \(2009\)](#) and others), one of the most interesting papers seems the one of [LECHMAN and LU \(2008\)](#) for the two following reasons: (i) they considered two uneven-sized spheres and (ii) the approximation of the toroidal model is explored in terms of the accuracy of the liquid volume; this last point is important for our current work.

We assume here that all grains are spherical and that the interface shape is a tore. This is a good approximation if the two spheres touch each other, or if the spheres are close enough (thin meniscus) – see figure 5. Although total curvature is not constant on the interface, the geometric properties are easy to compute. This model can be parameterized by both a gap distribution between the spheres and the contact angle (*to our knowledge, nobody has ever taken into account the adsorbed water film onto the spheres*). A remarkable result is that when a gap exists between

the spheres, then κ has no value for very small α_l (see figure 6) – in other words, liquid meniscus cannot be attached between two grains if the available liquid volume is too small. This latter fact can lead to difficulties during the numerical computation of the problem.

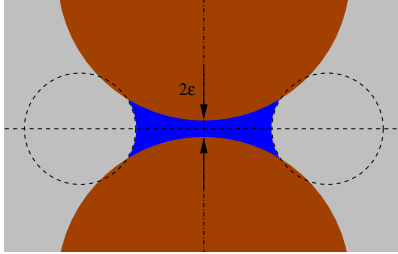


Figure 5: Toroidal model for a liquid meniscus between two spheres, with a prescribed contact angle at the solid boundary (schematic view at pore scale – liquid in blue, gas in light gray). The model can be parameterized by the gap 2ε between the grains.

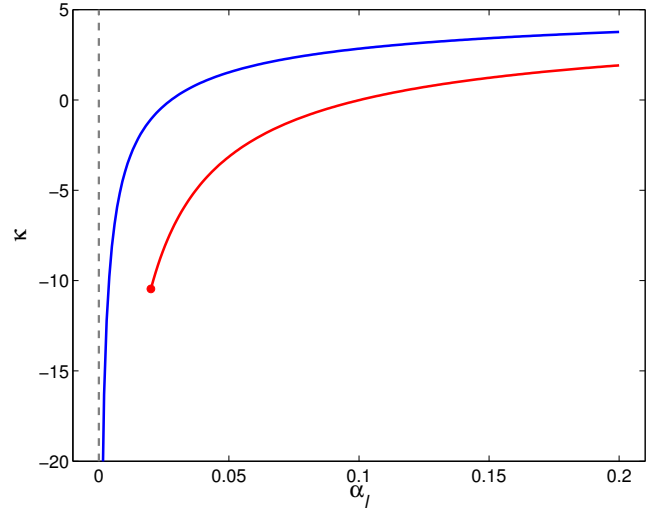


Figure 6: Liquid fraction / curvature relation, corresponding to figure 5: case $\varepsilon = 0$ (contact between the spheres – blue curve), and case $\varepsilon > 0$ (no contact between the spheres – red curve). The drawn curves just show the behavior, they don't come from realistic computation.

- an improved model which verify the mechanical equilibrium of the interface of the liquid menisci at the pore scale. The computation of the exact axisymmetric shape of a meniscus gives, after integration, the value of the volume. Knowing that this relation is stored in a finite set of discretized

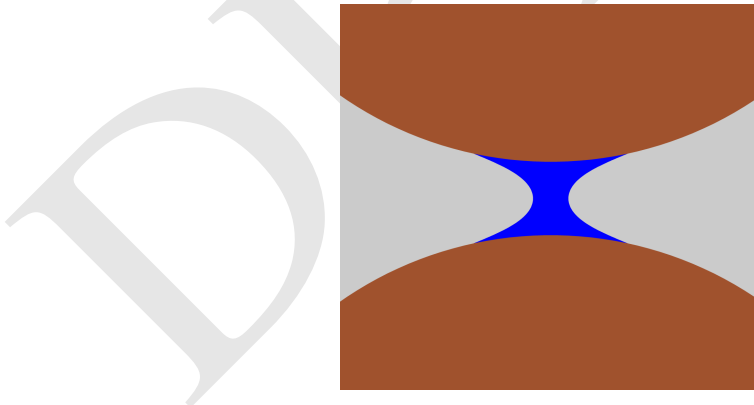


Figure 7: Contrary to figure 5, this is the exact shape of an axisymmetric meniscus. It can be easily seen that the meridian curve is far from a circle: it looks rather like a parabola.

values of α_l and κ , the relation 12 can be reconstructed by interpolation. The relation between α_l and κ not only may be not defined for some range of α_l (for the same reason as explained previously about the toroidal model) but should reveal a hysteretic behavior due to the breaking of the menisci during the evaporation. Again, this could lead some challenges in the numerical implementation. Taking into account the statistical distribution of the gaps in the granular medium should remove (*sure?*) the hysteretic behavior.

CANOT et al. (2015a) have been worked recently on this topic. This latter work is similar to the

numerical/regression laws found first by [MIKAMI et al. \(1998\)](#) when the grain have all the same radius, and extended later on by [SOULIÉ et al. \(2006\)](#) for a polydisperse granular material. While these authors aimed at computing the mechanical forces between two grains linked by a liquid bridges, a part of their results could be reused here, because curvature and water volume was of primary importance.

Each of these models is able to provide the interfacial area (needed for a non-equilibrium condition at the interface). This interfacial area writes:

$$F_4(\alpha_l, S_{w,I}) = 0$$

where $S_{w,I}$ is the interfacial area density, *i. e.* the interfacial area of the menisci per unit volume.

2.5 Additional equations

Diffusion of water vapor into air

We use the Fick law to describe how water vapor diffuses through air. Let's begin by the usual situation in free space, then lastly we shall adapt the equation for a porous medium. The Fick's law writes ([BIRD et al., 2002](#)):

$$\mathbf{j}_w = -\rho_g D_{w,a} \nabla \left(\frac{\rho_w}{\rho_g} \right)$$

where \mathbf{j}_w is the net mass flux of vapor through the stagnant gas mixture. $D_{w,a}$ is the diffusion coefficient between air and vapor. In our model, this latter coefficient is taken as a constant, while for sure it depends both on temperature and concentration values. Literature gives useful approximated relations for these dependances ([BIRD et al. \(2002\)](#), [NELLIS and KLEIN \(2009\)](#) and also many other books).

The Fick law is restricted here to the concentration diffusion. Theoretically, other terms should be added, as thermal diffusion (also known as Soret effect, while this latter name should rather be used for diffusion in liquids) or pressure gradient diffusion. These additional terms will be ignored here, because they are usually small; in our case, an estimation of the ratio of the thermodiffusion to the concentration diffusion leads to a numerical value of the order of 1/10. (*see the document entitled [thermodiffusion_estimation.pdf](#)*)

The net mass flux \mathbf{j}_w is related to the vapor velocity by the formula:

$$\mathbf{j}_w = \rho_w \mathbf{v}_w^*$$

where \mathbf{v}_w^* is the diffusion velocity of the vapor component with respect to the mass average velocity of the gas mixture:

$$\mathbf{v}_w^* = \mathbf{v}_w - \mathbf{v}_g$$

In porous media, the diffusion mechanism is the same (assuming that the characteristic length of the pores is not too small), except that the diffusion coefficient must be changed. The final equation used will be therefore:

$$\frac{\rho_w}{\rho_g} \mathbf{v}_w^* = -D_{w,e} \nabla \left(\frac{\rho_w}{\rho_g} \right) \quad (13)$$

The $D_{w,e}$ coefficient (an *effective* value for the diffusion coefficient through the porous medium) plays a role similar to λ_e ; theoretically, its determination may be hard, because it depends on the geometrical configuration, *i. e.* on the pores network's topology. The simplest approach consists in assuming that the effective value is derived from the physical one by multiplying it by a constant:

$$D_{w,e} = \tau_s D_{w,a}$$

τ_s is the tortuosity factor of the solid matrix (BIRD et al. (2002), LU and LIKOS (2004)); it is a positive dimensionless number less than unity because the diffusion in a porous medium is slower than that in free space. Some authors, like DAÏAN (1988), take this factor as a constant (*il semble y avoir une erreur dans l'approximation faite par J.-F. Daïan : il choisit $\tau_s = 0.5$ alors que les études de Currie (1960) indiquent plutôt que $\tau_s = 0.5 \phi$, ce qui est différent*), while ROSE (1963) explains that τ_s can be modelled as a function of the porosity ϕ , and gives few practical laws. By using the figure 1 of CURRIE (1960), we can estimate the following linear relationship for sands:

$$\tau_s \approx 0.884 \phi - 0.098$$

This relationship violates the constraint proposed by ROSE (1963), that is to say $\tau_s|_{\phi=0} = 0$, but in our case it will be used only for a range of porosity such that the tortuosity coefficient is non negative.

(Je n'aime pas trop ce coefficient de tortuosité; il semblerait plus rationnel de considérer une diffusion effective, un peu comme on fait pour la conduction thermique en milieu hétérogène). In the special situation where the pores network is constituted by parallel tubes, then $\tau_s = \phi$.

Spatial dispersion of one component due to the network structure of the porous matrix (geometrical effect) is not yet taken into account here (for sure, its relative effect with respect to the diffusion mechanism depends on the application). *(Pensez à mettre un terme de dispersion, proportionnel à la vitesse du gaz...)*

Effective thermal conductivity

(A similar section could be written concerning the effective diffusion coefficient $D_{w,e}$)

Many choices exist for the effective thermal conductivity λ_e :

- most of authors, as MIN and EMMONS (1972), take this variable as a constant. Although it is the simplest choice, it is evident that it is wrong.
- a different, reasonable choice is to take empirical relations found in literature. For example, equation (10) of CHEN (2008) (see also Figure 8):

$$\lambda_e(\phi, \alpha_l) = 7.5^{1-\phi} 0.61^\phi [(1.0 - 0.0022)\alpha_l + 0.0022]^{0.78\phi}$$

or equation [1-5] of SMITS et al. (2010) (see also Figure 9):

$$\lambda_e(\phi, \alpha_l) = Ke(\lambda_{\text{sat}} - \lambda_{\text{dry}}) + \lambda_{\text{dry}}$$

where Ke is the normalized thermal conductivity, also called the Kersten number. This number lies in the interval $[0, 1]$ and depends on the water content θ via the following formula:

$$Ke = \frac{\xi \theta}{1 + (\xi - 1) \theta}$$

where ξ is a dimensionless empirical fitting parameter, which is typically ranged from 5 to 30. The water content θ is the ratio of the liquid volume to the total volume so it is equal to $\phi \alpha_l$.

- another possibility is to choose semi-analytical models. For example, OKAZAKI (1985) derives the effective thermal conductivity considering grains as perfect spheres consolidated by liquid bridges. Note that this latter work is specially devoted to the apparent mass transfer coefficient in the adsorptive porous solid.
- it is worth noting that MOYNE et al. (1988) distinguish the true thermal conductivity of the medium (related to the Fourier law) and the apparent thermal conductivity which includes evaporation/condensation phenomena.

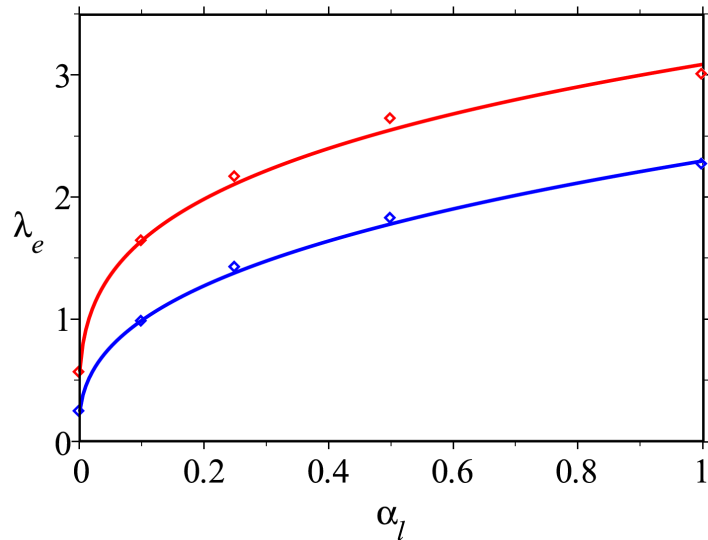


Figure 8: From Figure 9 of CHEN (2008). Red and blue data correspond respectively to $\phi = 0.354$ and 0.472 . Individual markers represents experimental data whereas continuous lines is the approximated relation. (Curves have been redrawn because it seems that there is a mistake in the published figure 9)

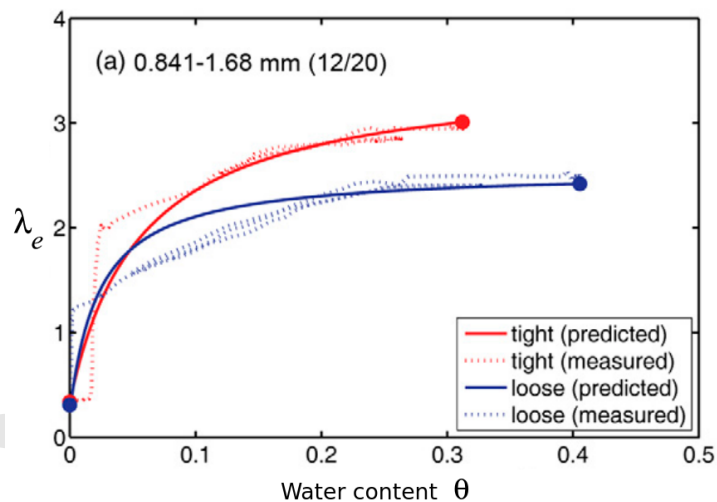


Figure 9: From Figure 7a of SMITS et al. (2010). Predicted and measured values of the thermal conductivity of a sand with grain sizes ranged in $0.841 - 1.68 \text{ mm}$. Red and blue curves correspond to different packing (porosity is resp. equal to 0.312 and 0.403). Notice that the prediction is good for great values of water content, but it is pretty poor for small values.

- while some authors present sophisticated models (CÔTÉ and KONRAD, 2005), we choose, in a last approach and for consistency with the liquid meniscus layout, a hysteretic relation already sketched by CANOT et al. (2015b); but this implies to add to our set of unknowns a boolean variable (both in x and t) which indicates whether the local meniscus is in the “contacting” state or in the “non-contacting” state (see also MAEDA et al. (2003)). Moreover, the results must be generalized to account for the statistical distribution of gaps between the grains.

2.6 Limitations of the current model

L-a) thermodynamical equilibrium is supposed to be verified at the microscale (pore scale); this implies that both temperature and water vapor density are uniform. However, vapor is created at the liquid interface, and heat is locally absorbed in the vicinity of the interface (latent heat).

In case of rapid evaporation/condensation processes, this assumption is violated. This may affect the heat and mass transfer at the macroscale, due to some delay effects.

L-b) in a granular media containing water under the pendular regime, all liquid menisci have a concave total curvature, leading to an internal liquid pressure lower than the surrounding pressure (Young-Laplace equation). The smaller menisci have a high curvature, therefore the liquid pressure level can be very low, perhaps even negative; in such a case, the liquid may be vaporized because the vaporization temperature decreases with the pressure, thus we should get $\alpha_l = 0$ (i.e. absolutely dry medium) whereas in the current model, $\alpha_l > 0$. However, negative pressure in liquids is not impossible (MACHIN (2002), or CHARLAIX and CICCOTTI (2010), p. 12-3). *Mais dans le cas d'un liquide loin des parois, ce sont des états métastables, non ? Peut-on dire que dans un ménisque, on obtient des états stables parce qu'on est extrêmement proche des parois solides, à savoir quasiment dans le film adsorbé ?*

The consequences for the numerical application of this model to a practical problem are the following:

C-a) when assuming the equilibrium at the pore scale, the temperature must vary slowly throughout the whole domain; in particular, this eliminates a thermal shock at a boundary.

C-b) ???

3 Numerical strategy

The set of equations (1-13) are composed of both Partial Differential Equations and algebraic equations. We chose to discretize first with respect to the spatial variables only (this is sometimes called "method of lines"). The new semi-discretized system is therefore a Differential Algebraic system of Equations (DAE), which can be solved using an automatic dedicated solver.

Difficulties come from the need of the Jacobian of the DAE system, because the BDF scheme used is an implicit scheme. Getting (or computing) the jacobian matrix may be difficult, especially when the equations are not continuous or not defined for all values of the variables' range.

A — A **first** numerical simulation *will consider*:

- (i) equilibrium condition at menisci's interface. This implies, as previously mentioned, slow variations in time, therefore slow forcing at boundaries.
- (ii) an asymptotic toroidal meniscus model (ATMM) with $\theta = 0$, in order to have both a simple relation for the equation 12 and liquid water present everywhere in the domain (so that α_l is never zero and equation 9 is easier to implement);
- (iii) a constant value for the thermal conductivity λ_e , like MIN and EMMONS (1972);
- (iv) an idealized packing where all spheres touch each other. All the gaps between two neighboring spheres are therefore zero (think, e. g. , the hexagonal compact arrangement of spheres).

B — Same configuration as case **A**, except that a non-equilibrium condition at interfaces is considered (equation 10).

C — A **third** numerical simulation *will be focused* on the numerical treatment of the twofold equation 9 whose form belongs to the complementarity problem:

$$\begin{cases} \text{if } a > 0 & \text{then } b = 0 \\ \text{otherwise, if } a = 0 & \text{then } b > 0 \end{cases}$$

which is equivalent to:

$$\min(a, b) = 0$$

This equivalence has been used by MARCHAND et al. (2013); BEN GHARBIA and JAFFRÉ (2014) and many other authors.

Moreover:

- (i) the flat meniscus model is chosen, so that equation 12 reduces to the trivial equation

$$\kappa = 0$$

and function $F_1(T, \kappa)$ in equation 9 is always equal to 1;

- (ii) again, the thermal conductivity λ_e is a constant;
- (iii) the sphere packing doesn't matter.

D — The **full** implementation (it combines both **B** and **C**) of the presented model *will account for*:

- (i) according to the class of boundary conditions (the forcing terms may be slow or not), the menisci's interface is considered under equilibrium or not;
- (ii) the full equation 9, treated as a complementarity problem;
- (iii) the true meniscus model, which comes from the exact integration for the interface shape;
- (iv) a reasonable law for the thermal conductivity λ_e ;
- (v) a reasonable sphere packing, obtained by DEM. We may envisage the two different packings used in CANOT et al. (2015a). One of them is parameterized by the mean gap and the width of its statistical distribution (Cauchy law).

Moreover, we should add the quick disappearance of the liquid meniscus by vaporization as soon as the liquid pressure drops below $p_{w, \text{sat}}$ (during evaporation, the meniscus curvature becomes more and more large – negatively – thus the liquid pressure decreases due to the Young-Laplace equation).

Mais quel serait alors le taux d'évaporation ? Peut-on prendre la loi du taux d'évaporation pour une interface hors équilibre ? (équation de Hertz-Knudsen, provenant de la dynamique moléculaire AJAEV (2012), p. 149)

Most of thermodynamics properties for water and air are taken from tables which can be found in an appendix of CENGEL and BOLES (2007).

Même avec ces cas simples, il me semble utile de regarder de près ce qui se passe sous l'effet d'un gradient thermique constant, en supposant que la température ne varie plus (en cours...). Plusieurs études (ainsi qu'un raisonnement simple) montrent que l'humidité migre vers les zones les plus froides...

Peut-on également envisager de considérer ρ_g comme uniforme, comme le font Min & Emmons ? On peut aussi envisager de prendre p_g comme constant, la vitesse des gaz résultant uniquement de la conservation de la masse...

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