Pore-scale investigation of dynamic effects on the moisture retention curve during spontaneous imbibition

Michele Bianchi Janetti¹,² and Hans Janssen²

¹University of Innsbruck, Unit for Energy Efficient Buildings, Technikerstrasse 13, 6020 Innsbruck, Austria.
²KU Leuven, Department of Civil Engineering, Building Physics and Sustainable Design, Kasteelpark Arenberg 40, 3001 Leuven, Belgium

michele.janetti@uibk.ac.at

Abstract. The moisture retention curve of porous materials is often assumed to be independent of the process dynamics, i.e., of the drying/wetting rate. Experimental outcomes and pore-scale simulations put this assumption into question though. It has been shown that dynamic effects can significantly affect the moisture retention curve, which presents different behaviours, depending on whether it is determined at transient or steady-state conditions. The cause of this phenomenon is addressed as “dynamic effects” in the literature. While dynamic effects of the drainage process have been widely studied, the data concerning spontaneous imbibition are still quite limited. We attempt at reducing this lack of knowledge by modelling spontaneous imbibition in an artificial material sample represented by a pore network model. In our model, the liquid flow is described via the Hagen-Poiseuille equation, while a percolation algorithm controls the dynamics of liquid-gas interfaces through the network junctions. A dynamic contact angle between liquid water and pore surface is considered, depending on the velocity of the meniscus. Dynamic states are determined by linking the local capillary pressure to the local moisture content in the artificial material sample subject to spontaneous imbibition. Our investigation demonstrates that dynamic effects due to contact angle variations may have a major impact on the imbibition process.

1. Introduction

Moisture is often the critical factor when judging built structures’ durability and sustainability, for which the accurate understanding and reliable assessment of moisture transfer and storage in building materials are crucial. The moisture storage capability of porous materials during any imbibition or drainage process is described via the moisture retention curve, a mathematical correlation expressing the local capillary pressure as a function of the local moisture content. This correlation is often assumed to be independent of the imbibition/drainage speed, i.e., the (de)saturation rate. In other words, any moisture retention curve determined under steady-state conditions is generally accepted to hold under transient conditions as well. Experimental outcomes and pore-scale simulations put this assumption into question though. In fact, it has been shown that the (de)saturation rate can significantly affect the moisture retention curve. The cause of this phenomenon, still not fully explained, is addressed in the literature as “dynamic effects” on the moisture retention curve.
An analysis on potential causes of dynamic effects is reported, e.g., in [1,2]. According to these studies, dynamic effects may impact the imbibition moisture retention curve as qualitatively illustrated in Figure 1: at a same capillary pressure, the moisture saturation is lower in the dynamic case relative to the steady-state case. Various other works suggest dynamic effects being related to the fluid properties (viscosity, density, surface tension), the material properties (porosity, pore size distribution) and the pore surface wettability (contact angle between fluid and solid). While dynamic effects of the drainage process have been widely studied, e.g. in [3], the data concerning spontaneous imbibition are still quite limited. This study aims at reducing this lack of knowledge by simulating spontaneous imbibition in a randomly-generated pore network which represents an artificial material sample. Our investigation focuses on the influence of contact angle variations on the imbibition process. We establish that dynamic contact angle variations occurring at the pore scale due to meniscus deceleration may significantly impact the pore scale capillary pressure and hence the moisture retention curve.

2. Impact of the dynamic contact angle on the capillary pressure
In this section we introduce a relationship linking the pore scale capillary pressure to the dynamic contact angle. We consider as exemplary geometry the partially saturated slit enclosed by two parallel plates shown in Figure 2. Capillary pressure $p_c$ is defined as the pressure drop across the meniscus:

$$ p_c = p_w - p_{nw} $$

Here, $p_w$ and $p_{nw}$ denote the pressure in the wetting and non-wetting phase (liquid water and air), respectively. The capillary pressure can be expressed as a function of the slit thickness and contact angle via the well-known Young-Laplace equation:

$$ p_c = -\frac{2\sigma \cos(\theta)}{h} $$

Here $\sigma$ denotes the surface tension of the wetting fluid [N/m], $h$ the slit thickness [m] and $\theta$ the contact angle [°] which the liquid forms with the solid surface. This contact angle may vary depending on the motion of the meniscus. Experimental pore-scale investigations have shown that during imbibition the contact angle increases with increasing meniscus velocity $v$. At equilibrium (i.e., for a static meniscus) the contact angle assumes its minimum value $\theta_e = \theta_d(v = 0)$, denoting $\theta_d(v)$ the contact angle of the advancing meniscus (dynamic contact angle).

Several relations for $\theta_d(v)$ based on hydrodynamic and molecular-kinetic approaches are reported, e.g. in [4,5]. The effects of viscosity and surface tension are equally considered in both approaches, any increase in bulk viscosity or decrease in surface tension leading to slower meniscus velocity. In other words, in both approaches the meniscus velocity results to be proportional to the ratio between the driving force, and viscosity.

![Figure 1](image1.png) Exemplary moisture retention curves for a steady state and transient imbibition process. The deviation between the steady state and transient curve is due to dynamic effects.

![Figure 2](image2.png) Slit formed by two parallel plates containing a wetting fluid 1 and a non-wetting fluid 2. Dotted line: meniscus during spontaneous imbibition; solid line: meniscus at equilibrium.
This effect of viscosity and surface tension is reflected in the following empirical correlation [4]:

\[
\cos(\theta_d) = \cos(\theta_e) - A \left(1 + \cos(\theta_e)\right) \left(\frac{\eta v}{\sigma}\right)^B
\]  \hspace{1cm} (3)

Here \(v\) denotes the velocity of the advancing meniscus [m/s] and \(\eta\) the dynamic viscosity of the wetting fluid [Pa s]. In this work we use Eq. (3) to describe the relationship between contact angle and meniscus velocity, although the proposed approach can be easily adapted to any other \(\theta_d(v)\) correlation.

In Eq. (3) \(\theta_e\), \(A\) and \(B\) are empirical parameters which must be determined by fitting experimental data. Some results concerning imbibition experiments performed with liquid water as wetting fluid are reported in Figure 3. In [4], measurements concerning imbibition in glass tubes of internal diameter varying from 0.5 to 1.3 mm are reported. For meniscus velocities up to 0.6 m/s, a fair agreement was found with \(\theta_e = 0^\circ\), \(A = 2\) and \(B = 0.5\). Note that the analysis included data on several wetting fluids besides liquid water which are not reported here. This explains the imperfect fit of the blue curve in the graph. Further experiments on different wetting fluids including liquid water were carried out in [5] with glass capillaries of sizes varying from 100 to 250 µm and meniscus velocities up to 0.0012 m/s. In that study, optimal agreement was found by applying \(\theta_e = 30^\circ\), \(A = 4.2\) and \(B = 0.51\). In [6] the imbibition of liquid water in quartz capillaries of radii varying from 45 to 272 nm was considered. In contrast with the works cited above, contact angles were observed to be velocity-dependent for \(v < 5\) µm/s, while being nearly constant above that value. We found that the experimental data reported in [6] can be fairly fitted with Eq. (3) by assuming \(\theta_e = 30^\circ\), \(A = 700\), \(B = 0.5\). The major deviation of the coefficient \(A\) from the above values can be explained considering the drastically smaller radii of the considered capillaries and the resultantly far lower meniscus velocities analyzed in the latter study.

In general, it must be noted that any \(\theta_d(v)\) relationship suffers from a limited validity, depending on the meniscus velocity and capillary size, and has to be carefully chosen according to the range of interest of these parameters. Additional consideration shall be made concerning the equilibrium contact angle which characterizes the wettability of the solid surface when the meniscus velocity approaches the zero. Considering moisture transfer in porous media where silica is the dominant material, \(\theta_e = 0^\circ\) is often assumed. This assumption may however be inappropriate for materials as calcite, dolomite, coal, and talc [3,7], surfaces coated with natural organic material, or surfaces that have been exposed to surfactants or NAPLs [3,8].

From Eqs. (2) and (3) one obtains the dynamic pore scale capillary pressure \(p_{c,d}\) as a function of the slit thickness and velocity of the meniscus as follows:

\[
p_{c,d}(h, v) = p_{c,e}(h) \left[1 - A \frac{1 + \cos(\theta_e)}{\cos(\theta_e)} \left(\frac{\eta v}{\sigma}\right)^B\right] \hspace{1cm} (4)
\]

with \(p_{c,d}(h, 0) = p_{c,e}(h)\) defining the equilibrium (static) pore scale capillary pressure.

\[\text{Figure 3. Dynamic contact angle measured by Heshmati et al. [4], Li et al. [5] and Sobolev et al. [6]. The measured values are fitted with Eq. (3) (solid lines).}\]
3. Pore network model

In order to investigate the effect of the contact angle variation on the imbibition process, a pore network model, similar to the one described in [9], has been set up. Such model represents an artificial porous material, in which capillary driven moisture flow occurs. The network nodes are located on a two-dimensional cartesian grid, connected by throats of equal length which are in fact gaps enclosed between infinitely extended parallel plates, as shown in Figure 4. The pressure gradient in the non-wetting phase (air), as well as phase change processes (evaporation and condensation) at the water-air interface are hence disregarded.

Piston flow is imposed in each (partially) filled throat. Assuming laminar flow, the momentum equation reduces to the plane Hagen-Poiseuille’s law and the liquid flow through the throat $ij$ can be described by the following equation:

$$ j_{ij} = -\frac{\rho h_{ij}^{2} \Delta p_{ij}}{12\eta l_{ij}} $$

(5)

Here, $j_{ij}$ denotes the flux of liquid water [kg/(m²s)] through the throat $ij$, $l_{ij}$ the length of the liquid column in the throat $ij$, $\rho$ the density of liquid water [kg/m³], $h_{ij}$ the thickness of the throat [m] and $\Delta p_{ij}$ the pressure drop across the liquid column. For completely filled throats $l_{ij} = 2L$, 2$L$ being the distance between two neighboring nodes. The spatial pressure distribution in the network at the time $t$ is hence determined by solving a system of equations derived from the liquid water conservation at each node. For each water filled node $i$, the mass conservation is given by:

$$ \sum_{j=1}^{4} h_{ij} j_{ij} = 0 $$

(6)

$h_{ij}j_{ij}$ being the moisture flows [kg/(m s)] from and to the node. To proceed to the next time step $t + \Delta t$, the menisci positions are updated by calculating the advancing distance $\delta_{ij}$ [m] of each meniscus as follows:

$$ \delta_{ij} = -\frac{h_{ij}^{2} (p_{c,ij} - p_{i})}{12\eta l_{ij}} \Delta t. $$

(7)

Here $p_{i}$ denotes the pressure [Pa] at the node $i$, $p_{c,ij}$ the capillary pressure [Pa] and $l_{ij}$ the length of liquid column in the throat $ij$. All these quantities are determined at the time $t$.

Figure 4. i-th element located in a network composed by n columns. Each element presents 4 throats of thickness $h_{ij}$. Two neighbouring throats in adjacent network elements are forced to have the same thickness, i.e, for each throat $ij$ holds: $h_{i1} = h_{(i-n)4}$; $h_{i2} = h_{(i-1)3}$; $h_{i3} = h_{(i+1)2}$; $h_{i4} = h_{(i+n)1}$.
The new length is then explicitly calculated as follows:

\[ l_{ij}(t + \Delta t) = l_{ij}(t) + \delta_{ij}(t). \] (8)

Note that, according to Eq. (4), the capillary pressure \( p_{c,ij} \) depends on the meniscus velocity, which is given by:

\[ v_{ij} = \frac{\delta_{ij}}{\Delta t}. \] (9)

The invasion algorithm is completed by a few rules which control the meniscus propagation: 1) when the liquid front reaches an empty node, this is activated by setting the liquid length in the neighbouring throats to a small value \( l_{ij0} \) just before evaluating the new pressure distribution (in the case study shown below, \( l_{ij0} = L/40 \) gives fair results in terms of mass conservation); 2) if in a throat the driving pressure difference \( p_i - p_{c,ij} \) is negative, the meniscus is arrested until such pressure difference becomes positive again; 3) when two menisci meet, they merge (i.e., air entrapment is disregarded).

4. Case study

The pore network approach is tested by simulating spontaneous imbibition in an artificial material sample. This material sample is composed by 10 equal elementary cells placed on top of each other, each cell including 10 x 10 square network elements of side \( 2L = 20 \) [µm]. Each network element is composed by four throats connected to a central node, as shown in Figure 4. The throat thicknesses are randomly assigned from a generalized extreme value distribution.

In Figure 5 the throat thickness distribution in the sample, as well as the probability density and cumulative probability of throat thickness are shown. The network elements placed at the sample bottom are in contact with the water reservoir, while impermeable boundary conditions are imposed at both long sides of the sample. Imbibition occurs according to the invasion algorithm described above.

![Figure 5](image-url)
5. Results

Two test cases have been considered to investigate the spontaneous imbibition behavior of the artificial material sample. Firstly the contact angle is assumed to be constant during the entire imbibition process, i.e., equal to the static (equilibrium) contact angle ($\theta_e = 30^\circ$ is assumed). Secondly the contact angle varies as a function of the meniscus velocity, according to Eq. (3), with $\theta_e = 30^\circ$; $A=2$ and $B=0.5$. The capillary pressure and moisture saturation distributions (mean values of each row) obtained with a constant (static) contact angle are reported in Figure 6 (a) and (c), respectively, while the same physical quantities obtained with variable (dynamic) contact angle are reported in Figure 6 (b) and (d).

In the dynamic case, one observes a delay of the imbibition process with respect to the static variant, i.e., the capillary pressure and moisture saturation profiles are shifted to the left. This is consistent with the dynamic contact angle being larger than the static one, thus leading to a smaller capillary pressure and slower imbibition process. In Figure 6 (e) the moisture saturation distributions obtained with a constant (static) contact angle are plotted against the Boltzmann variable: $\lambda = x t^{-1/2}$. It can be observed that the moisture saturation profiles collapse into a single curve, as predicted by diffusion theory [10,11]. On the contrary, a spread between the moisture saturation profiles is observed when the contact angle varies with the meniscus velocity, as illustrated in Figure 6 (f). In this case the process cannot be captured with the classic diffusion equation, which in fact requires local thermodynamic equilibrium.

Figure 6. Capillary pressure and saturation distributions obtained with the pore network model with (a)(c) constant (static) contact angle $\theta = \theta_e = 30^\circ$ and (b)(d) variable (dynamic) contact angle ($A=2$; $B=0.5$; $\theta_e = 30^\circ$) at $t1=1.1$; $t2=3.3$; $t3=6.5$; $t4=10.0$ [ms]; saturation expressed as function of the Boltzmann variable $\lambda = x t^{-1/2}$ for (e) static contact angle and (f) dynamic contact angle.
The capillary pressure values linked with corresponding moisture saturation values, i.e., determined at the same time and location, are reported in Figure 7. These “dynamic” states are compared with the steady-state moisture retention curve, i.e., determined for an infinitely slow imbibition process over an elementary cell. It can be observed that the values obtained by dynamic pore network simulation are in agreement with the steady-state moisture retention curve when a constant (static) contact angle is applied. On the contrary, the dynamic states are clearly shifted to the left side when applying a variable contact angle. The deviations between dynamic states and steady state curve are larger at early times, gradually reducing the more the imbibition process moves forward.

![Figure 7](image)

**Figure 7.** Steady state moisture retention curve and results from dynamic pore network simulations obtained with (a) constant (static) contact angle $\theta = \theta_e = 30^\circ$ and (b) variable (dynamic) contact angle ($A = 2; B = 0.5; \theta_e = 30^\circ$) at $t_1 = 1.1$ ms; $t_2 = 3.3$ ms; $t_3 = 6.5$ ms; $t_4 = 10.0$ ms.

6. Conclusions
We have simulated the spontaneous imbibition process in porous materials via a pore network approach. The proposed model takes into account pore scale contact angle variation due to deceleration of the meniscus. Thus our investigation considers the impact of such contact angle variation on the capillary pressure and moisture saturation distributions in an artificial sample, as well as the related dynamic effects on the moisture retention curve. We found that dynamic effects appear to be negligible when a constant (static) contact angle is applied, while they are important for processes including variable (dynamic) contact angles. Further simulation and experimental work is required to determine the influence that such dynamic effects may have on the moisture transfer at the macroscopic scale and under real boundary conditions, as well as for characterization of the dynamic contact angle in real building materials.

Acknowledgements
The authors wish to acknowledge the financial support from the “Austrian Science Fund” (FWF), Erwin Schrödinger Fellowship, project number: J 4213-N30. The computational results presented here have been achieved (in part) using the LEO HPC infrastructure of the University of Innsbruck. The authors also wish to thank Daan Deckers, Staf Roels and Emanuela Bianchi Janetti for fruitful discussions.

References
[1] S. M. Hassanizadeh and W. G. Gray, “Mechanics and thermodynamics of multiphase flow in porous media including interphase boundaries,” vol. 13, no. 4, pp. 169–186, 1990.
[2] S. M. Hassanizadeh, “A Theoretical Model of Hysteresis and Dynamic Effects in the Capillary
Relation for Two-phase Flow in Porous Media,” no. 1, pp. 487–510, 2001.

[3] D. M. O. Carroll, K. G. Mumford, L. M. Abriola, and J. I. Gerhard, “Influence of wettability variations on dynamic effects in capillary pressure,” Water Resour. Res., vol. 46, 2010.

[4] M. Heshmati and M. Piri, “Experimental Investigation of Dynamic Contact Angle and Capillary Rise in Tubes with Circular and Noncircular Cross Sections,” Langmuir, vol. 30, no. 47, pp. 14151–14162, 2014.

[5] X. Li, X. Fan, A. Askounis, K. Wu, and K. Se, “An experimental study on dynamic pore wettability,” Chem. Eng. Sci., vol. 104, pp. 988–997, 2013.

[6] V. D. Sobolev, N. V. Churaev, M. G. Velarde, and Z. M. Zorin, “Surface Tension and Dynamic Contact Angle of Water in Thin Quartz Capillaries,” J. Colloid Interface Sci., no. 222, pp. 51–54, 2000.

[7] W. G. Anderson, “Wettability literature survey. 1. Rock-oil-brine interactions and the effects of core handling on wettability,” J. Pet. Technol., vol. 11, no. 38, pp. 1125–1144, 1986.

[8] J. L. Ryder and A. H. Demond, “Wettability hysteresis and its implications for DNAPL source zone distribution,” J. Contam. Hydrol., no. 102, pp. 39–48, 2008.

[9] S. Gruener, Z. Sadjadi, H. E. Hermes, A. V. Kityk, K. Knorr, and S. U. Egelhaaf, “Anomalous front broadening during spontaneous imbibition in a matrix with elongated pores,” vol. 109, no. 26, pp. 10245–10250, 2012.

[10] J. Crank, The Mathematics of Diffusion. Oxford University Press, 1975.

[11] M. Bianchi Janetti and P. Wagner, “Analytical model for the moisture absorption in capillary active building materials,” Build. Environ., vol. 126, 2017.