ANALYSIS OF CONTACT ANGLE IN CAPILLARY INVASION

Michael Frederico Paiva da Silva
UFSC
LMPT, Campus Universitário, Trindade
Florianópolis, Santa Catarina, CEP 88040-900, P.O. Box 476
fredpaiva@lmpt.ufsc.br

Rodrigo Surmas
UFSC
LMPT, Campus Universitário, Trindade
Florianópolis, Santa Catarina, CEP 88040-900, P.O. Box 476
surmas@lmpt.ufsc.br

Luís Orlando Emerich dos Santos
UFSC
LMPT, Campus Universitário, Trindade
Florianópolis, Santa Catarina, CEP 88040-900, P.O. Box 476
emerich@lmpt.ufsc.br

Paulo César Philippi
UFSC
LMPT, Campus Universitário, Trindade
Florianópolis, Santa Catarina, CEP 88040-900, P.O. Box 476
philippi@lmpt.ufsc.br

Abstract. *The correct knowledge of the physical processes that control the fluid-fluid interface displacement at the pore-level is of increasing interest due to the growing possibility of direct simulation of immiscible displacement offered by the strong development of computers' performance and numeric methods and to the increasing accuracy in three-dimensional reconstruction methods. Flow of immiscible fluids is, classically, treated by considering that the transition layer has a null thickness. In this way, in addition to intrinsic physical properties of the involved fluids, the only macroscopic parameter of interest is the interfacial tension. At microscopic level, when two immiscible fluids are mixed, the long-range attraction between the molecules of each fluid is the molecular mechanism promoting fluid segregation. The thickness of transition layer is, consequently, controlled by the strength and length of long-range potentials and by the binary diffusivity. Theoretical difficulty is strongly increased when these two fluids interact with a solid surface. In fact, the interfacial energies between the fluids and the surface are the main macroscopic mechanisms governing interface advancing or receding on a solid surface. In present work, a lattice Boltzmann model is presented and used for studying the dynamic effects on the contact angle produced by interface displacement.*

Keywords*: immiscible displacement, contact angle, lattice Boltzmann model*

1. Introduction

Capillaries have many applications in different areas like the microelectronics and petrochemical industries. Also they are used in capillary pumps in aerospace industries. In the petroleum exploration, its extraction is strongly influenced by capillary effects inside the reservoir.

The necessity of understand these or other applications of capillaries at modern industry take us to the study of wetting phenomena on solid surfaces and their behavior in ideal capillaries that, in spite of certain simplifications, still represent well the real model. The model can be validated through comparisons between theoretical results found in the literature and results obtained through numeric simulations.

Usually, the description of immiscible fluids flux is performed from a momentum and mass balance around the interface, disregarding its thickness. In this way, besides the properties of each fluid, there is just an additional parameter, the interface tension. When these fluids are in contact with a solid surface, the difficulty increases sensibly. Normally, the characterization is completed by a contact angle measured between the fluid-fluid interface and solid. However, it is insufficient to know only the value of the equilibrium angle. For a complete description, the form that the angle will assume, with different velocities, in imbibition and drainage processes, has to be known. Beyond the difficulty in obtaining, or preview, the angle variation form, it is complicated to have this, even when the interface is in equilibrium, because the angle can be affected by impurities, by the interface position according to the gravity force applied and also due to the surface roughness (de Gennes, 1985).

From a microscopic point of view, the interface is a result of attractive long-range forces acting on inside of each fluid. In this case, the interface tension reflects range and intensity of forces involved. In the same way, also the contact angle becomes a consequence of interactions that occur on a microscopic level. Then, the angle depends of the fluid-fluid and fluid-solid interactions. Therefore, the fluids' and interfaces' characterization is given by microscopic parameters like long-range forces and potentials of fluid-solid attraction. This kind of approach can be appropriated for processes simulation which capillarity is relevant, because the contact angle dynamic effects don't have to be known *a priori*. These effects have to appear as a consequence of the model dynamics.

The capillary rise dynamics was first described by Lucas and Washburn in 1921, balancing capillary, viscous and gravitational forces and a parabolic profile of velocities. Although experimental data confirm its validity to imbibition in long capillaries, this equation fails because it doesn't consider inertial effects (Kornev and Neimark, 2001). Based on this study, Bosanquet proposed an alternative equation in 1923. However, the Bosanquet equation doesn't consider the effects at the flow entrance. After rederive its equation, considering two fluids with the same viscosity and density, Santos *et al*. found the following equation to the meniscus height (Santos, Wolf and Philippi, 2004)

$$\frac{d^2h(t)}{dt^2}+\frac{(D^2-1)\mu}{r^2\rho}\frac{dh(t)}{dt}=\frac{(D-1)\sigma\cos\theta}{r\rho H}-\frac{gh(t)}{H} \tag{1}$$

where $D = 2$ for two dimensions (parallel plates) and $D = 3$ for a cylindrical capillary. The other parameters, σ, θ, g e H, are, respectively, interface tension, contact angle, gravity acceleration and capillary length.

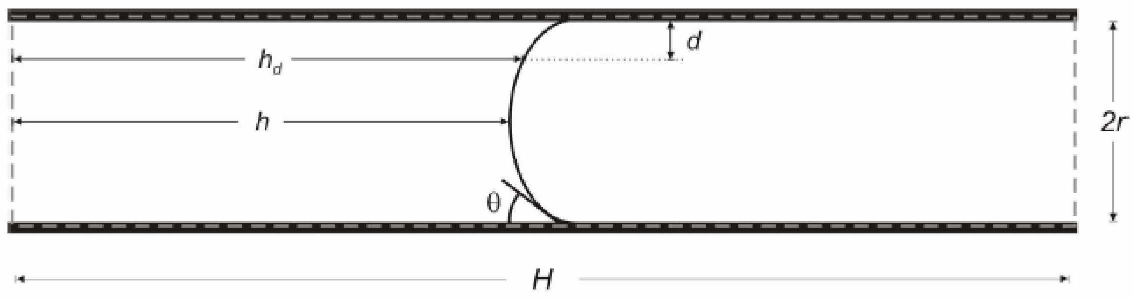

Figure 1. Parameters to measure the contact angle, θ.

In Fig. (2), the contact angle and its behavior in imbibition and drainage processes is shown. Contact angle represents a wetting measure and it can be measured geometrically.

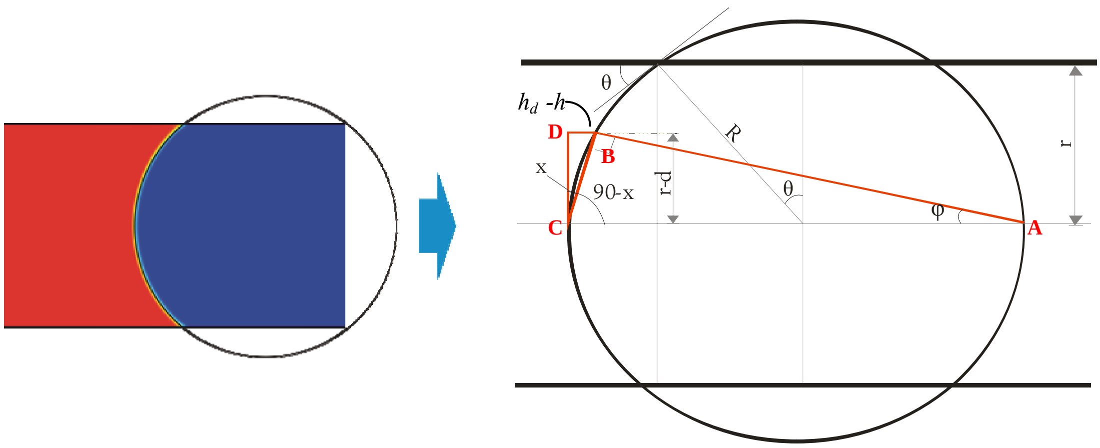

Figure 2. Parameters to measure the contact angle, θ.

Equaling the sum of ABC triangle angles in Fig. 2 to 180º, it is easy proving that $x = \varphi$. Applying sine definition in this triangle, the next equation can be found

$$sen\varphi=\frac{\sqrt{(r-d)^2+(h_d-h)^2}}{2R}$$

If $x = \varphi$, the sine definition is also applied to BCD triangle and replacing its result in the last equation, resulting in:

$$\frac{(h_d - h)}{\sqrt{(r-d)^2 + (h_d - h)^2}} = \frac{\sqrt{(r-d)^2 + (h_d - h)^2}}{2r/\cos\theta}$$

Rearranging it, the equation below is found. This will return the contact angle directly from simulated data (Santos, Wolf and Philippi, 2004).

$$\cos\theta = \frac{2r(h_d - h)}{(r-d)^2 + (h_d - h)^2} \tag{2}$$

An interesting feature, which will be analyzed after simulations, is the difference between contact angles of imbibition and drainage, named contact angle hysteresis. This difference can be great, easily being over than 10º in not specially prepared surfaces. Generally, this hysteresis is caused by superficial roughness, contaminants on the surface or solutes like surfactants or polymers mixed with fluid, but can be caused simply by capillary forces or by the necessary pressure to displace the interface in the same or opposite direction of spontaneous invasion.

2. Lattice Boltzmann Method

The Lattice Boltzmann Method (LBM) is a hydrodynamic model of simulation based on Kinetic Theory, that is much appropriate to the resolution of wetting and capillary invasion problems considered here. This method appeared in the end of the decade of 80 as an extension of the Lattice Gas model (Lattice Gas Automata). The LBM used in the simulations is a variant of a LBM based on field mediators (Santos, Facin and Philippi, 2003), described in (Santos, Wolf and Philippi, 2004).

2.1. Lattice Boltzmann Method for two-phase flow

The phase segregation, such as occur in immiscible fluids, is a result of long-range interaction of particles of each fluid. Field mediators were used to introduce these interactions in the model. The mediators carry information about concentration of each fluid. From these information is possible modify the collision process, simulating the long-range interaction effect. For this, the collision operator is separated in two terms, in which one is responsible for the single-phase interaction and the other one is responsible for the two-phase interaction. The long-range interactions are included in the second term, since they are important only when occur in more than one fluid, excepting to phase transition, not boarded in this work.

Describing formally the information of last paragraph, four distribution functions will be used, each one representing the two types of particles and their respective mediators, $N_i^{\psi}(\vec{X},T)$ and $M_i^{\psi}(\vec{X},T)$, where ψ = *r,b* represents the type of fluid. Mediator dynamics can be described by equation

$$M_i^{\psi}(\vec{X} + \vec{c}_i, T+1) = \frac{\rho^{\psi}(\vec{X},T)}{\rho^r(\vec{X},T) + \rho^b(\vec{X},T)} \tag{3}$$

The velocity of mediators $\vec{u}^m$ is defined as

$$\vec{u}^m(\vec{X},T) = \sum_i M_i^r(\vec{X},T) - M_i^b(\vec{X},T) \tag{4}$$

Remembering the long-range interactions are expressed by changes in particle velocities, *modified velocities* are defined by mediator action.

$$\vec{v}^r = \vec{u}^r - A\frac{\vec{u}^m}{|\vec{u}^m|} \tag{5}$$

$$\vec{v}^b = \vec{u}^b - A\frac{\vec{u}^m}{|\vec{u}^m|} \tag{6}$$

where the parameter A is related to the interaction intensity and, consequently, to the interfacial tension.

The interaction between fluid particles is represented by a split collision operator. Considering a single-phase flow, the main collision effect is to relax the N_i distribution towards a prescribed equilibrium distribution N_i^{eq}, which can be described by macroscopic parameters as density and velocity, using a BGK operator

$$\Omega_i^{\alpha\beta} = \frac{N_i^{eq} - N_i}{\tau^{\alpha\beta}} \tag{7}$$

with the relaxation time represented by $\tau^{\alpha\beta}$ and related with the fluid viscosity that will be simulated.

Then, the particle dynamics can be stated in the form

$$N_i^{\psi}(\vec{X}+\vec{c}_i, T+1) = N_i^{\psi}(\vec{X},T) + \left(\frac{\rho^{\psi}}{\rho^r + \rho^b}\right)\Omega_i^{\psi\psi}(\vec{X},T) + \left(\frac{\rho^{\overline{\psi}}}{\rho^r + \rho^b}\right)\Omega_i^{\psi\overline{\psi}}(\vec{X},T) \tag{8}$$

where the single-phase operator $\Omega_i^{\psi\psi}$ is reproduced by Eq. (7) (ψ = *r or b*). Although, the two-phase operator $\Omega_i^{\psi\overline{\psi}}$ also can be written in Eq. (7) form (ψ = *r or b*, $\psi \neq \overline{\psi}$), the equilibrium distribution has to be calculated with modified velocities according to Eqs. (5) and (6). The utilization of different relaxation times for each fluid allows the simulation of fluids with different viscosities. The relaxation time τ^{rr} refers to the interactions between particles in the wetting fluid, τ^{bb} in non-wetting fluid and τ^{rb} in the interface.

3. Procedures and simulations

For the contact angle study, imbibition and drainage simulations were performed in a D3Q19 lattice (DmQn, m – Euclidean dimension, n – number of velocities). It was used the following parameters τ^{rr} = 1,5, τ^{bb} = 1,0 and τ^{rb} = 1,0, A = 0,4, α = 0 and β = 1, and $\rho^r = \rho^b$ = 1,0. The capillarity was the main effect involved in imbibition, but in some simulations a very low positive pressure gradient was applied, favoring the displacement, with intention to become them faster. To drainage, a contrary pressure gradient was applied, winning the capillary forces and forcing the wetting fluid to leave the capillary.

Some simulations had been realized varying this pressure gradient, observing the wetting effect of the surface and the contact angle presented. With the Eq. (3), it is possible to find the contact angles in any point of the capillary where the interface is.

Then, simulations involving rough surface were realized using same parameters of smooth surface, however only qualitative results were obtained, because calculating the contact angle with equation (3) is incorrect due to the instantaneous changes of the angle of the surface because of the roughness and wetting of the surfaces.

4. Results

From simulations in smooth surface the angles presented in Tab. 1 were obtained. The contact angle decreases in drainage as the pressure gradient increase, whereas the angle stays constant in imbibition due to the only effect of capillarity acting in the displacement. Comparing Figs. 3 and 4, it is evident the difference of angles in the two processes. This occur because, forcing the flow, the fluid tends to move itself like in Poiseuille flow, where there is a no slip condition, for which the fluid hold on the surface, tending to wet it.

The contact angle hysteresis (the difference among imbibition and drainage angles) can be observed in Fig. 5. It is observed two levels where each one represents a process. The upper level contains imbibition angles and the lower level contains drainage angles. The vertical lines are transition periods.

Table 1. Contact angles for smooth surfaces.

$\Delta p_{drainage}$	$\Delta p_{imbibition}$	$\theta_{drainage}$	$\theta_{imbibition}$
0,014	0,0	39,99º	69,08º
0,015	(-)[1]	40,75º	-
0,020	0,0	14,52º	69,07º
0,020	(-)[1]	26,08º	-

[1]: Imbibition hasn't been performed.

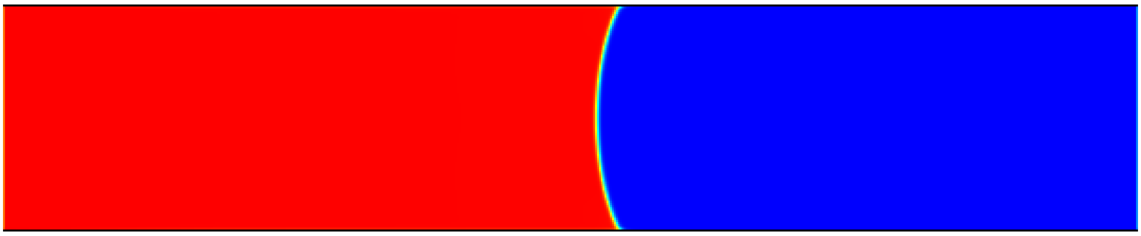

Figure 3. Imbibition of a fluid in a smooth capillary.

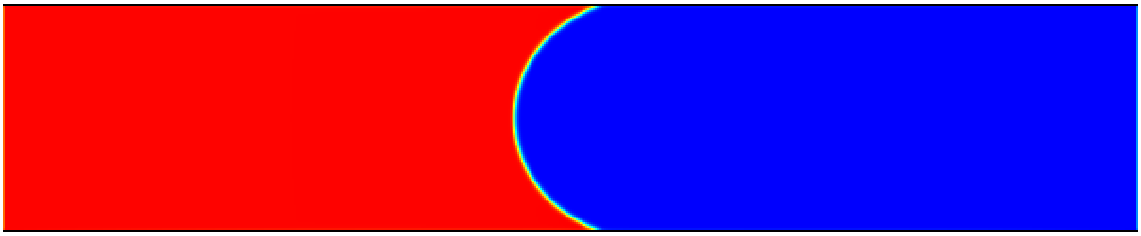

Figure 4. Drainage of a fluid in a smooth capillary. Note the difference of contact angle among Figs. 3 and 4.

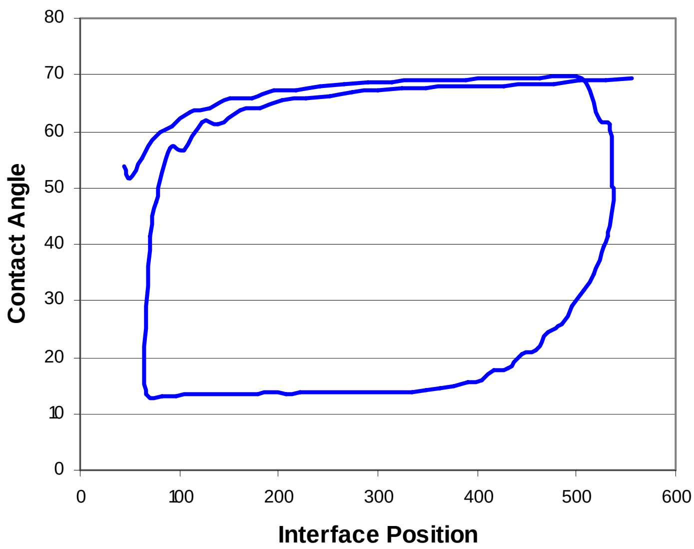

Figure 5. Contact angle hysteresis.

The capillary invasion in rough surface reflects better the reality, since in the physical world there are no completely smooth surfaces. To use the Eq. (2), it would have to find the instantaneous angle of each point and just later finding the real contact angle, what it would be very difficult, beyond that the lack of symmetry of the walls confers the interface an asymmetrical appearance also becoming complicated to foresee the format it will assume in the next instant. However, a visual evaluation is so adequate. Note in Fig. 6 the wetting on the walls during a drainage process, which is caused for the excess of irregularities in this region, where the fluid has a very low speed, due to the no slip condition, staying imprisoned in some points of the surface, assuming the aspect of a real wet wall.

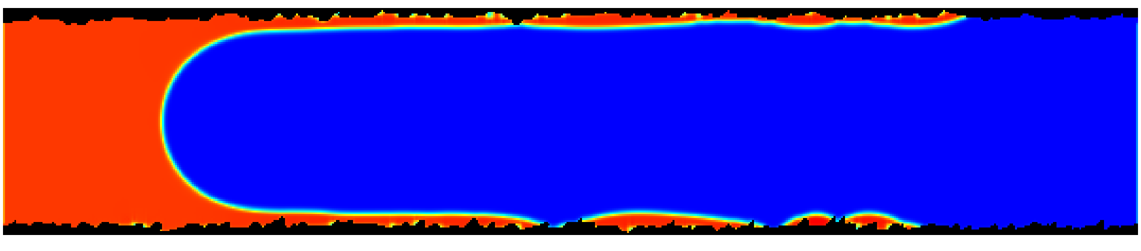

Figure 6. Capillary invasion for a rough surface.

5. Conclusions

In this work it is considered the use of Lattice-Boltzmann model for immiscible fluids and, in special, in capillary invasion processes. A model with three relaxation times was used, allowing the control of the viscosities and diffusivity in a independent way.

In the studied problem, the main difficulty involving simulations of capillary invasion is the contact angle variations as a consequence of the invasion dynamics and inertial effects. Thus, we foresee that the lattice Boltzmann model can be capable to predict these contact angle variations, becoming an alternative tool in study of invasion processes.

However, although the obtained results agree well to qualitative expectations, more studies still are necessary, bringing out the analysis of boundary conditions, and comparison with experimental data, to evaluate the range in which the model is suitable to simulate these kind of processes.

6. Acknowledgements

We acknowledge the support by CNPq, Finep and ANP for the opportunity to participate and to collaborate in the development of this project.

7. References

de Gennes, P. G. Wetting: statics and dynamics. Rev. Mod. Phys., v. 57, n. 3, p. 827-863, 1985.

dos Santos, L. O. E.; Philippi, P. C. Lattice-gas model based on field mediators for immiscible fluids. Phys. Rev. E, V.65 (4): Art. No. 046305, 2002.

Kornev, K. G.; Neimark, A. V. Spontaneous penetration of liquids into capillaries and porous membranes revisited. J. Colloid. Interf. Sci. 235 (1), p. 101-113, 2001.

Santos, L. O. E.; Facin, P. C.; Philippi, P. C. Lattice-Boltzmann model based on field mediators for immiscible fluids. Phys. Rev. E, V.68 (5): Art. No. 056302, 2003.

Santos, L. O. E.; Wolf, F. G.; Philippi, P. C. Dynamics of interface displacement in capillary flow. Submitted to Journal of Statistical Physics, 2004.