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Après avis de :

Mme	Isabelle CANTAT	Rapporteur
Mme	Marie-Caroline JULLIEN	Rapporteur

Devant la commission d'examen formée de : :

Mme.	Annie COLIN	Directrice de thèse
M.	Hugues BODIGUEL	Co-directeur de thèse
M.	Pierre JOSEPH	Examineur
M.	Mikel MORVAN	Président
M.	José BICO	Invité

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Introduction

An oil is any substance that is liquid at ambient temperatures and does not mix with water but may mix with other oils and organic solvents. This general definition includes vegetable oils, volatile essential oils, petrochemical oils and synthetic oils. Some oils burn in liquid or aerosol forms, generating heat which can be used directly or converted into other forms of energy such as electricity or mechanical work. To obtain many fuel oils, crude oil is pumped from the ground and is shipped via oil tanker to an oil refinery. There, it is converted from crude oil to diesel fuel (petrodiesel), ethane (and other short-chain alkanes), fuel oils (heaviest of commercial fuels, used in ships/furnaces), gasoline (petrol), jet fuel, kerosene, benzene (historically), and liquefied petroleum gas. A 42 gallon barrel (U.S.) of crude oil produces approximately 10 gallons of diesel, 4 gallons of jet fuel, 19 gallons of gasoline, 7 gallons of other products, 3 gallons split between heavy fuel oil and liquified petroleum gases and 2 gallons of heating oil. The total production of a barrel of crude oil into various products results in an increase to 45 gallons [1, 2].

The oil is located under the earth and is captured in the small pores of the rocks. The sizes of the throats are very polydisperse and range between a few hundred nanometers to a few micrometers. Fractured regions comprise channels of a few centimeters. To recover oil, wells are constructed. The oil well is created by drilling a hole into the earth with an oil rig. A steel pipe (casing) is placed in the hole, to provide structural integrity to the newly drilled wellbore. Holes are then made in the base of the well to enable oil to pass into the bore. Finally a collection of valves called a "Christmas Tree" is fitted to the top, the valves regulating pressures and controlling flows. During the primary recovery stage, reservoir drive comes from a number of natural mechanisms. These include: natural water displacing oil downward into the well, expansion of the natural gas at the top of the reservoir, expansion of gas initially dissolved in the crude oil and gravity drainage resulting from the movement of oil within the reservoir from the upper to the lower parts where the wells are located. Recovery factor during the primary recovery stage is typically 5-15%.

While the underground pressure in the oil reservoir is sufficient to force the oil to the surface, all that is necessary is to place a complex arrangement of valves (the Christmas tree) on the well head to connect the well to a pipeline network for storage and processing.

Over the lifetime of the well the pressure will fall, and at some point there will be insufficient underground pressure to force the oil to the surface. After natural reservoir drive diminishes, secondary recovery methods are applied. They rely on the supply of external energy into the reservoir in the form of injecting fluids to increase reservoir pressure,

hence replacing or increasing the natural reservoir drive with an artificial drive. Sometimes pumps, such as beam pumps and electrical submersible pumps (ESPs), are used to bring the oil to the surface. Other secondary recovery techniques increase the reservoir's pressure by water injection, natural gas reinjection and gas lift, which injects air, carbon dioxide or some other gas into the bottom of an active well, reducing the overall density of fluid in the wellbore. Typical recovery factor from water-flood operations is about 30%, depending on the properties of oil and the characteristics of the reservoir rock. On average, the recovery factor after primary and secondary oil recovery operations is between 35% and 45%.

Tertiary, or enhanced oil recovery methods increase the mobility of the oil in order to increase extraction.

Thermally enhanced oil recovery methods (TEOR) are tertiary recovery techniques that heat the oil, thus reducing its viscosity and making it easier to extract. Steam injection is the most common form of TEOR, and is often done with a cogeneration plant. In this type of cogeneration plant, a gas turbine is used to generate electricity and the waste heat is used to produce steam, which is then injected into the reservoir. This form of recovery is used extensively to increase oil extraction in the San Joaquin Valley, which has very heavy oil, yet accounts for 10% of the United States oil extraction. In-situ burning is another form of TEOR, but instead of steam, some of the oil is burned to heat the surrounding oil [3].

Chemical compound can also be used in tertiary recovery. The Company Rhodia is working actively on this approach. The subject of my PhD is linked to this project.

The injection of various chemicals, usually as dilute solutions, have been used to improve oil recovery. Injection of alkaline or caustic solutions into reservoirs with oil that has organic acids naturally occurring in the oil will result in the production of soap that may lower the interfacial tension enough to increase production. Injection of a dilute solution of a water soluble polymer to increase the viscosity of the injected water can increase the amount of oil recovered in some formations. Dilute solutions of surfactants such as petroleum sulfonates may be injected to lower the interfacial tension or capillary pressure that impedes oil droplets from moving through a reservoir. Special formulations of oil, water and surfactant, microemulsions, can be particularly effective in this. Application of these methods is usually limited by the cost of the chemicals and their adsorption and loss onto the rock of the oil containing formation. In all of these methods the chemicals are injected into several wells and the production occurs in other nearby wells.

The use of viscous solution of polymers allows also to improve oil recovery. Polyacrylamide molecules of high molecular weight are injected to increase the amount of oil recovered in China. This improves the sweeping of the oil. This avoids instability of the propagation of the interface between polymer solutions and oil. The number of water preferential paths towards the outlet well is decreased. The sweeping is more efficient. More over the increase of the water viscosity avoid the trapping of the oil. Microbial injection is part of microbial enhanced oil recovery and is presently rarely used, both because of its higher cost and because the developments in this field are more recent than other techniques. Strains of microbes have been both discovered and developed (using gene mutation) which function either by partially digesting long hydrocarbon molecules,

by generating biosurfactants, or by emitting carbon dioxide.

The aim of the Company Rhodia is to develop surfactants solutions to increase the amount of recovered oil. In order to reach this aim, the reasons for oil trapping have to be elucidated and understood. One needs to define functioning points in terms of required viscosity, required interfacial tension, required wetting properties. The formulations have to be adapted to these values but they have also to be stable in a wide range of temperature and in a wide range of salt concentrations.

The subject of my PhD deals with an academic work in relation with this project. We want to understand why so little amount of oil is produced during the second recovery. We look for the microscopic factors in charge of the existence of an unstable and ramified front between water and oil. One of the major difficulties in achieving a good description of biphasic flows in interconnected network is the large number of parameters potentially involved. These include the viscosity of the two fluids, the interfacial tension between them, the wetting properties, their respective flow rates, the topology of the network and the considered length scales.

To capture the phenomena involved in this process, two approaches are commonly developed. One is a macroscopic approach and deals at the level of the porous media. The second one is a microscopic approach and deals with the flow at the level of the pores of the rocks. In the following, we will use the second approach. In the next section, we will recall briefly how it is possible to characterize the features of the flow at the porous media level. Then we will describe the physical principles that rule the flow at the pore level. We will display a brief overview of the open questions and discuss the questions we will address.

Flow in porous media

Engineers use Darcy laws to model the flow of a liquid in a porous media [4]. Forgetting all the details of the porous media structure they assume that the flow rate per unit of volume q of a Newtonian fluid in a porous media is related to the drop of pressure through a linear relation:

$$\vec{q} = -\frac{K}{\eta}(\vec{\nabla}P - \rho g) \quad (1)$$

where g is the gravity, ρ the density, K the Darcy constant, η the viscosity of the newtonian fluid. K depends upon the geometry of the porous media.

This equation captures the flow of Newtonian fluids provided that the Reynolds number (*i.e.* the ratio between the inertial and the viscous forces) is low and provided that the porous media is not altered by the flow.

This approach becomes trickier when one wants to apply it to biphasic flows.

Indeed, due to Laplace law, the drop of pressure between two phases is equal to

$$P_o - P_w = \gamma\left(\frac{1}{r_a} + \frac{1}{r_b}\right) \quad (2)$$

where γ is the interfacial tension between the two fluids, r_a and r_b the two radii of curvature of the interface and P_o and P_w respectively the pressure in the oil phase and in the water phase.

We recall that the interfacial tension γ is the energy required to create an interface of unit area between the two liquids. The presence of interfaces between the two fluids induces pressure jumps. These pressure jumps make the Darcy analysis difficult. It is usually admitted that the flow rate of water q_w and the flow rate of oil q_o remain proportional to the drop of pressure in each fluid. Engineers write:

$$\frac{\vec{q}_w}{S} = -\frac{Kk_{rw}}{\eta_w} \cdot \vec{\nabla} P_w \quad (3)$$

$$\frac{\vec{q}_o}{S} = -\frac{Kk_{ro}}{\eta_o} \cdot \vec{\nabla} P_o \quad (4)$$

where S is the surface perpendicular to the flow, k_{rw} the relative water permeability, k_{ro} the relative oil permeability, P_w the pressure in the water phase, P_o the pressure in the oil phase, η_w the water viscosity and η_o the oil viscosity. k_{rw} and k_{ro} are functions of S_o and S_w , which are the oil and water saturation. S_o and S_w respectively measure the volume of oil and water compared to the total volume available.

Mass conservation leads to:

$$S_o + S_w = 1 \quad (5)$$

$$\phi \frac{\partial S_w}{\partial t} + \frac{\partial q_w}{\partial x} = 0 \quad (6)$$

$$\phi \frac{\partial S_o}{\partial t} + \frac{\partial q_o}{\partial x} = 0 \quad (7)$$

where ϕ is the porosity of the porous media.

To close the system, one equation is missed. The two pressure fields may be linked by assuming that $P_w - P_o = P_c(S_w)$, where k_{rw} , k_{ro} and $P_c(S_w)$ are measured in separate experiments on sample of rocks. The previous set of equations allows one to predict the flow at the reservoir level.

This macroscopic approach is very usefull but it does not give us informations about the features of the fluid we have to inject in order to increase the amount of recovered oil. These parameters are hidden in the relative water or oil permeability, or in the evolution of P_c as a function of S_w . To do such an analysis at the pore level is required.

Flow in micro-models

We jump at the pore scale and focus on the displacement of a wetting fluid by a more viscous non wetting one. In absence of viscous or gravity forces, the displacement (drainage) of a wetting fluid by a non-wetting fluid is solely governed by the capillary forces. They prevent the non-wetting fluid from spontaneous entering in the porous media. It can enter

a throat (of radius R) only when the pressure in the non-wetting fluid exceeds the pressure in the wetting fluid by a value of P_c , the capillary pressure given by $P_c = 2\gamma/R$, where γ is the interfacial tension. As a consequence, the fluid penetrates the pore throat, which has the largest size (the smallest capillary pressure) among the available ones. This process is successfully described by the invasion percolation (IP) model.

In the presence of both viscous and capillary forces, the pressure field is not uniform anymore. The viscous forces modify the difference of pressure between the two fluids and promotes the entrance of the invading fluid in the smaller throat.

In this case the displacement is characterized by two dimensionless parameters: the capillary number $Ca = \eta_1 V / \gamma$ and the viscosity ratio $M = \eta_1 / \eta_2$, where V is the velocity of the injected fluid, η_1 its viscosity, η_2 the viscosity of the displaced fluid, and γ the interfacial tension.

Lenormand has proposed a phase-diagram of drainage in porous media [5]. Their approach leads to an original display of the corresponding domains on a general diagram with axes of capillary number and viscosity ratio. Three regimes correspond to the limits when two of the three forces: capillary forces, viscous forces and pressure gradient, are negligible, as sketched in Figure 1.

For $M > 1$ at low capillary number, the zone separating the two fluids includes a front with open structures on many length scales surrounded by two compact structures (capillary fingering). As Ca increases, the front width decreases and leaves the place to a stable compact flow. These two propagation mechanisms can be captured using concepts from gradient percolation (*i.e.* introducing a pressure gradient in the two fluids). For $M < 1$, same picture holds for low capillary numbers. However, at high capillary numbers, viscous fingering causes an unstable displacement. These phenomena were experimentally evidenced using micromodels of porous media which allow a direct observation of the phases displacement.

The wetting situation (*i.e.* the nature of the rocks) has been much discussed in the literature [6] and seems an important issue in the oil enhanced recovery processes. Oil recovery in oil wet reservoir is more difficult than in water wet reservoir.

In order to understand this point, it is required to study the flow as a function of the wetting situation. We address this question in this PhD. Our aim is to understand how a meniscus between two liquids advances in a single throat of a porous media.

Outlines of the PhD

We want to study the displacement of liquid-liquid interfaces. In the literature, many geometries have been used to address this question. Spreading of a drop, raise of the meniscus in a capillary tube or on a vertical surface are examples of such geometries. In this work, we focus at the pore level and study the displacement of a liquid-liquid meniscus in a micro channels of circular or rectangular sections. We address the role of microscopic flows and corners films in this process.

Chapter 1 deals with a short presentation of wetting and spreading theories. We discuss

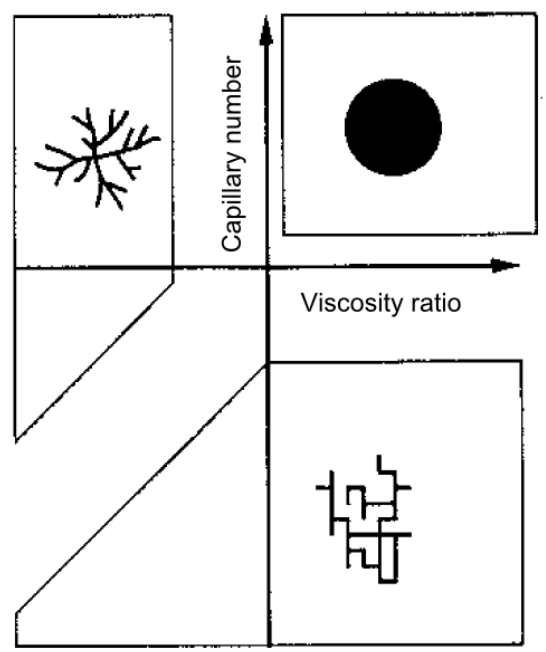


Figure 1: Original phase-diagram of Lenormand [5] in the drainage experiment for the displacement of a wetting fluid by another one. Three main regimes are illustrated through a general diagram with axes representing the capillary number and the viscosity ratio. These illustrations represent the injected fluid (black) from the center and the displaced one (transparent).

both the static and the dynamic properties. We present the microscopic films and the corner films.

Chapter 2 displays some methods of fabrications of microfluidic chips on PDMS, on glass and on resin SU-8.

Chapter 3 and 4 deal with the wetting dynamics in the drainage situation. We study the dynamics of liquid-liquid menisci in a circular tube at small capillary numbers in partial, pseudo-partial and complete wetting conditions. In the inner surface treated glass tube, there exists a thin wetting film in the last two situations. We control precisely the displacement of two immiscible liquids to observe the meniscus velocities and contact angles as a function of pressure gradient. Under pseudo-partial wetting condition, we observe that there is a pressure range where the velocity is extremely low (below $1 \mu\text{m/s}$) but non zero, in contrast with partial wetting, where the meniscus is blocked by a pinned contact line corresponding to the standard contact angle hysteresis. The role of surface heterogeneity is discussed to explain the observations. In the same pseudo-partial wetting system, special dynamic properties are also observed, which concerns various transient regimes of velocity after a prompt change of pressure gradient.

Then we focus on more complex geometry and we will analyze the role of the corner films. For a tube of arbitrary cross-section exhibiting corners, capillarity requires that

the wetting liquid remains along the corners. Liquid flows in these corner films. We experimentally investigate the role of these corner flows on the dynamics of a liquid-liquid meniscus, under complete wetting situation, by taking advantage of a microfluidic PDMS cross-junction. Our results show that there is a strong coupling between the corner flows and the meniscus displacement, when it lies in the vicinity of the junction (up to 10 times the channel width). Part of the observations is accounted for by a model based on a network of adaptive hydrodynamic resistances. Chapter 5 addresses this property.

Lastly, we design a special circle channel to study the consequences of corner flows in the drainage process under complete wetting situation. Wetting liquid clusters are trapped in the pore or in a porous media model. Here we demonstrate that trapped cluster of wetting fluid is drained by a new mechanism, which is different from the displacement by viscous forces. Under complete wetting situation, the trapped wetting liquid diminishes its volume gradually through the corners. We develop a model that captures the experimental data. It will be detailed in Chapter 6 and 7.

Summary

Flow in porous media:

- Darcy Law describes the flow of a liquid in a porous medium. It proceeds by averaging several properties and gives a global picture of the flow. The flow rate and the drop of pressure are described as a function of macroscopic features of the porous medium (porosity, permeability).
- For a flow between two immiscible fluids, the presence of interface induces the pressure jumps, which makes Darcy analyses difficult.

Flow in micro-models:

- At the pore scale, the displacement of a wetting fluid by a non-wetting one is characterized by two dimensionless parameters: the capillary number $Ca = \eta V / \gamma$ and the viscosity ratio $M = \eta_1 / \eta_2$. The capillary number is the ratio between viscous forces and capillary forces.
- According to Ca and M , viscous fingering, capillary fingering or a stable compact flow are observed during drainage.
- Experiments show that wetting properties play an important role in the oil recovery process.

The outline of this PhD

- We focus on the displacement of a meniscus between two liquids in micro channels of circular or rectangular sections.
- We study the wetting dynamics in complete, pseudo-partial and partial situations. We analyze our results in the framework of the thermally activated depinning theory. Under pseudo-partial wetting situation, the role of the wetting film on the wetting dynamics is analyzed.
- In a channel of arbitrary cross-section exhibiting sharp corners, we analyze the role of corner flows under complete wetting situation.
- The consequence of corner flows in the drainage process under complete wetting situation is studied in a loop.

Part I

State of the art

Chapter 1

Wetting

1.1 Introduction

A liquid, placed in contact with a solid, will flow to minimize its free energy. The flow will continue until the liquid attains a stable or possible metastable equilibrium configuration. This is a common wetting and spreading phenomenon, which occurs in various industrial areas. The liquid may be a paint, a lubricant, an ink or a dye. The solid may either show a simple surface or be finely divided (suspensions, porous media, fibers). At large scales, wetting or non-wetting plays an important role in oil recovery [7], the efficient deposition of pesticide on plant leaves [8], the drainage of water from highways [9] and the cooling of industrial reactors. At smaller scale, wetting solutions are proposed to solve technological problems in microfluidics and nanoprinting, inkjet printing, etc. [10]. There are also applications for the modification of surface properties. It could be chemical means to modify the surface chemistry (like plasma treatment [11], silanization [12]). It could be functional coating to modify the wetting properties, which means a deposit of thin film intended to generate some special properties (*i.e.*, antireflection, antifreezing, or antifouling). Generally speaking, wetting phenomena are an area where chemistry, physics, and engineering intersect.

These modifications of surface by "chemical" interactions act over the scales of molecules, which is often referred as short-ranged interactions. Surface forces such as Van der Waals or electrostatic forces are paramount for determining the wettability of a surface. Van der Waals surface forces, which is called "long-ranged", can still be important over distances corresponding to dozen of molecules, because their algebraic decay is rather slow.

In this chapter, we explain how to characterize different types of wetting, and their physical properties. Here the theories come from [13–19]. We also present wetting dynamics and hysteresis properties. These theories will help us to better understand the experimental results in this thesis work.

1.2 Wetting criteria

The wetting behavior of a liquid on a solid substrate is determined by the difference between the cohesive interactions holding the liquid and the adhesive interactions between the liquid and solid [20]. Here, we neglect the electrostatic interactions, since dodecane and silicon oil are electrically neutral. The interactions with a short-range repulsion and an algebraically decaying attraction can thus be related to the molecular interaction potentials, Lennard-Jones form [21].

$$u(r) = \epsilon \left[\left(\frac{r_0}{r} \right)^{12} - \left(\frac{r_0}{r} \right)^6 \right] \quad (1.1)$$

where r_0 and ϵ are positive constants, and r is the intermolecular distance.

The attractive term $u(r) \propto 1/r^6$ is dominated by the long-range interactions of van der Waals forces. This algebraic tail form adequately describes the London dispersion energy between non-polar molecules, the Debye energy between dipolar and non-polar molecules, as well as the Keesom energy between freely rotating dipolar molecules. There are other forces (e.g., hydrogen bonding, hydration forces, etc.) which are very short ranged and leads to exponentially decaying forces between interfaces rather than algebraic ones. Sharma and Jameel [22, 23] carried out a systematic study of the interplay between these short-ranged polar surface forces and the Lifshitz-van der Waals apolar forces (arising from $1/r^6$ potentials). They adopted the simplifying assumption that the apolar spreading parameter is simply proportional to the amplitude of the tail of the net apolar interaction between interfaces. Using the Young-Laplace and Navier-Stokes equations they related the stability properties of a thin adsorbed film to macroscopic wetting parameters such as the contact angle.

We consider a three-phase system. A liquid film of thickness h on a solid substrate. h is much greater than the range of molecular interactions, but enough thin to consider the contribution of long-range interactions to the energy balance. The third phase, which is the ambient phase, could be liquid or vapor. With a quite thin film on a solid surface with thickness h , the free energy of this film is of the form:

$$F(h) = \gamma_{sl} + \gamma + P(h) \quad (1.2)$$

where γ_{sl} is the solid-liquid's interfacial tension and γ the liquid-ambiance interfacial tension. $P(h)$ is an alternatively additional energy term, which should be described not only in terms of the intermolecular forces (van der Waals forces), but also many other components: dipole-dipole, hydrogen bonds, and various effects due to the anomalous density of the liquid near the wall [14]. At large h , $P(h)$ tends to zero. When h is larger than the molecular size a_0 , $P(h)$ is controlled by long range van der Waals forces

$$P(h) = \frac{A}{12\pi h^2}, a_0 \ll h \ll l \quad (1.3)$$

where A is the Hamaker constant of the system, which depends on the intermolecular constants in the presence.

As a result of this interaction potential on the wetting behavior, if the adhesive solid-liquid interactions are strong, the system can lower its free energy by increasing the distance h between the two surfaces. This leads to a net repulsive force per unit area between the solid-liquid and liquid-vapor interfaces, which is called the disjoint pressure $\Pi(h)$, accounted in the literature by the introduction of Derjaguin [24]

$$\Pi(h) = -\frac{dP(h)}{dh} \quad (1.4)$$

1.2.1 Hamaker constant

The Hamaker constant A is thus a key property for determining the wetting behavior, and can be calculated exactly [25], in terms of the dielectric properties of the three materials, where solid and vapor denote the material in the two half spaces, and liquid is the intermediate material. These materials are characterized by their frequency-dependent polarizability. In the "repulsive" case, in which the layer tends to thicken, we have $A > 0$.

For the above three phases system, the effective Hamaker constant can be calculated with Equation 1.5 [20]. The index 1, 2 and 3 refer to displacing fluid, displaced fluid and substrate.

$$A_{132} = -\frac{3}{4}k_B T \cdot \frac{\epsilon_1 - \epsilon_3}{\epsilon_1 + \epsilon_3} \cdot \frac{\epsilon_2 - \epsilon_3}{\epsilon_2 + \epsilon_3} - \frac{3h\nu_e}{8\sqrt{2}} \cdot \frac{(n_1^2 - n_3^2) \cdot (n_2^2 - n_3^2)}{\sqrt{(n_1^2 + n_3^2) \cdot (n_2^2 + n_3^2)} \cdot [\sqrt{n_1^2 + n_3^2} + \sqrt{n_2^2 + n_3^2}]} \quad (1.5)$$

where ϵ_i designates the relative permittivity of component i , n_i is its refraction index (values measured in the laboratory for the fluids and referred from the Handbook for the solid substrates: glass and cross-linked PDMS), k_B is the Boltzmann constant $1.381 \times 10^{-23} \text{ J.k}^{-1}$, T the atmosphere temperature 298 K , h is the Planck constant $6.626 \times 10^{-34} \text{ J.s}$ and ν_e is the adsorption frequency in the ultraviolet, equal to 10^{15} [26].

In Equation 1.5, the first term presents the integration of the dipolar interactions over all frequencies, and expresses them as an effective interaction between the two surfaces bounding the half spaces. It is given by the "zero frequency" dielectric constants of the materials, called zero-frequency or Keesom and/or Debye part.

The second term considers the main contribution to the integral. The frequencies corresponds to visible light. And consequently it is given by the refractive indices in the visible. It is called the dispersive or London part.

The Hamaker constant A is the sum of the two contributions given above. It also follows the second term that, for a symmetrical situation (two identical materials separated by a third and different material), the net effect of the van der Waals forces is always an effective attraction between the two interfaces ($A < 0$). Thus if only van der Waals interactions are important, two interfaces are attracted to each other and $V = 0$. In general, a wetting problem is different, as there are three different materials. In that case, it follows Equation 1.5 that depending on the dielectric properties of the three media, Hamaker constant A can have either sign.

1.2.2 Spreading parameter

For a system of three phases: vapor, solid, liquid, we introduce the spreading parameter S , defined by $S = \gamma_{sv} - (\gamma_{sl} + \gamma_{lv})$, which is the difference between the energy of a dried solid and that of a solid covered by a macroscopic layer of liquid [13] (γ_{sv} , γ_{sl} and γ_{lv} are the solid-vapor, solid-liquid and liquid-vapor interfacial tensions, respectively). The spreading parameter S is often determined using contact angle measurements of a drop of liquid on a solid surface in air, which will be detailed later.

If the three interfacial tensions and the Hamaker constant are known, the wetting state of the fluid follows directly. If $S < 0$ and regardless of the sign of A , a droplet with a finite contact angle minimizes the free energy of the system, and this is the partial wetting situation (detailed in Section 1.2.4). On the other hand, if $S \geq 0$, the contact angle is zero. This prohibits the formation of a wetting layer. Furthermore, if $S \geq 0$ and $A < 0$, a wetting layer will form, and the system will consequently be in equilibrium when a macroscopic uniform liquid film covers the whole solid surface. We speak of complete wetting (detailed in Section 1.2.3). If $S \geq 0$ and $A > 0$, an intermediate state may occur: pseudo-partial wetting (detailed in Section 1.2.5), which exhibits a coexistence of macroscopic contact angle and microscopic wetting film.

1.2.3 Complete wetting

In a classical vapor/liquid/solid system, the free energy $F(h)$ per unit area of a flat film of thickness h , pictured in Figure 1.1, is given by Equation 1.3, where we take S to be positive and A to be negative.

$F(h)$ may be a monotonically decreasing function (Figure 1.1(a)), or have a maximum (Figure 1.1(b, c)) at $h = h_m$. Then, for $h < h_m$, $\Pi(h)$ becomes negative. In any case above, the free energy minimum corresponds to a solid, wet by a thick film $h \rightarrow \infty$. This complete wetting is studied in detail in the review of P. G. de Gennes in 1985 [13].

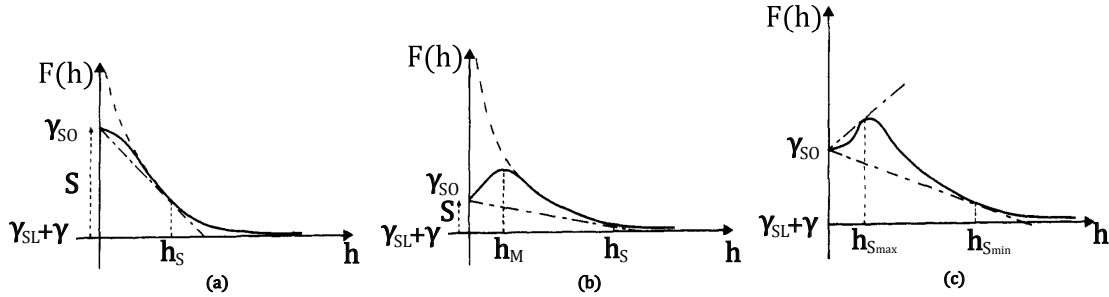


Figure 1.1: Qualitative plot of the free energy $F(h)$ of a film versus thickness h for S positive and A negative. (a) $F(h)$ is monotonously decreasing, (b) $F(h)$ has a maximum and one inflection point, (c) $F(h)$ has two reflection points. In all cases, $F(h)$ is minimal for $h \rightarrow \infty$, this corresponds to the complete wetting situation.

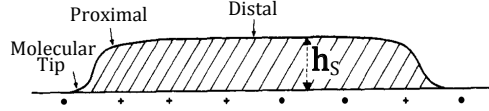


Figure 1.2: Final "pancake" in the case of complete wetting. Near the contact line, the profile is parabolic in the proximal region controlled by van der Waals energies and ends with a microtip reaching the solid surface with a horizontal slop. The solution $h_{s(min)}$ ($h_{s(max)}$) corresponds to a minimum (a maximum) of the energy $F(h)$.

In this wetting situation, a small droplet, put in contact with a flat solid surface, spreads out and becomes the thin "pancake", pictured in Figure 1.2. The thickness of this wetting film h results from a competition between S , which favors a large wet region and long-range forces, which tend to thicken the film. The tangent to the curve $F(h)$ in Figure 1.1 graphically constructs a threshold thickness h_s of "pancake", whose equation is given by:

$$P(0) = S = P(h_s) + h_s \Pi(h_s) \quad (1.6)$$

The droplet spreads and achieves a thin wetting film surrounded by a dry solid to minimize its energy. The films with thickness greater than h_s are stable, and with thickness less than h_s are metastable or unstable. This thickness is not always required small, when $S \ll \gamma$, this thickness is greater than a molecular film. Theoretically, a droplet under complete wetting spreads and achieves a wetting film of thickness h_s . With smaller S , the thickness is greater, as P and $h\Pi(h)$ tend to 0 when h becomes big. So a small S involves a thick wetting film.

1.2.4 Partial wetting

The negative spreading parameter S and positive or negative Hamaker constant A lead to partial wetting. The liquid droplet makes a finite contact angle on a dry solid, sketched in Figure 1.3, with corresponding free energy $F(h)$ in Figure 1.4.

When S is negative, the droplet does not spread and form a macroscopic contact angle θ with the substrate. This angle is noted θ_e in equilibrium, which is determined by the resultant between adhesive and cohesive forces. The contact angle provides a measure of wettability [27]: A contact angle $\theta_e < 90^\circ$ usually indicates that wetting of the surface is very favorable, and this is a hydrophilic surface. A contact angle $\theta_e > 90^\circ$ generally means that wetting of the surface is unfavorable and this is a hydrophobic surface.

For a liquid droplet on a solid substrate in Figure 1.5, three different phases are present: vapor, liquid and solid. Therefore there are three interfacial tensions needed to be considered: solid-liquid γ_{sl} , liquid-vapor γ_{lv} and solid-vapor γ_{sv} . The relation between the equilibrium contact angle θ_e and the three interfacial tension is given by Young's equation (1805) [28]:

$$\cos \theta_e = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \quad (1.7)$$

Practically, the spreading parameter of the vapor/liquid/solid system is measured by the γ_{lv} .

$$S = \gamma_{lv}(\cos\theta_{lv} - 1) \quad (1.8)$$

where $\gamma = \gamma_{lv}$ denotes the liquid-vapor interfacial tension.

For a liquid/liquid/solid system, the spreading parameter is defined when the three phases are in equilibrium (force balance) with each other. A simple combination of Young's law (see Equation 1.7) allows to deduce the value of S .

$$S = \gamma_{S1} - (\gamma_{S2} + \gamma_{12}) = \gamma_{2v}\cos\theta_{2v} - \gamma_{1v}\cos\theta_{1v} - \gamma_{12} \quad (1.9)$$

where, index 1 and 2 are the two liquids. Specially, for a water/oil/solid system, we have

$$S = \gamma_{air/oil}\cos\theta_{oil/solid} - \gamma_{air/water}\cos\theta_{water/solid} - \gamma = \gamma(\cos\theta_e - 1) \quad (1.10)$$

In a liquid/liquid/solid system, the droplet could be liquid A in liquid B or liquid B in liquid A on solid surface. Each situation leads to a spreading parameters S_1 or S_2 .

With this relation Equation 1.10, the θ_e can only be defined for negative S . The small spreading parameter S corresponds to a big contact angle θ_e , which means the surface is less wettable by this liquid.

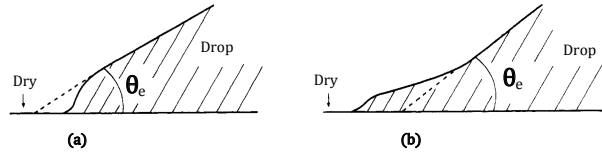


Figure 1.3: Final equilibrium of a droplet in the case of partial wetting. The solid around the droplet is dry: the profile is hyperbolic and curved downward if A is negative in (a) and upward if A is positive in (b).

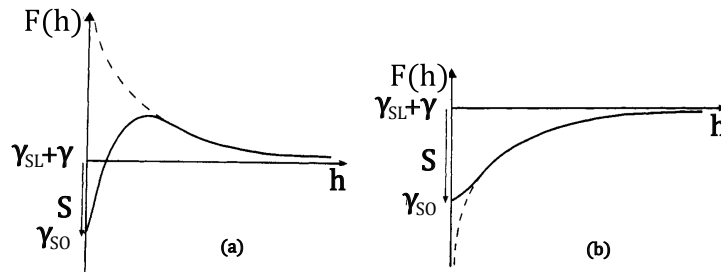


Figure 1.4: Free energy $F(h)$ corresponding to partial wetting. Both situation have negative S , but negative A in (a) and positive A in (b). $F(h)$ has no minimum at finite thickness.

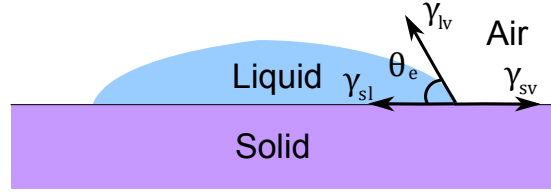


Figure 1.5: Young's relation is interpreted as a mechanical force balance on the three-phase contact line.

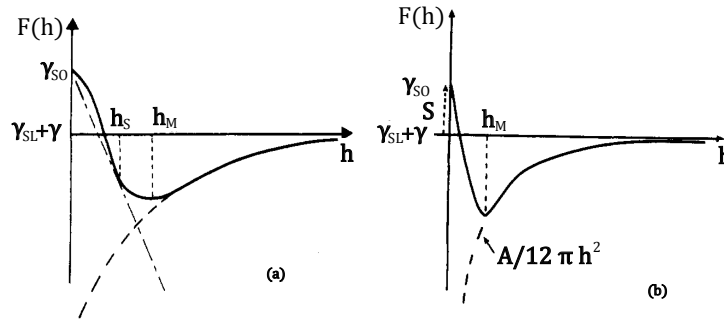


Figure 1.6: Free energy corresponding to pseudo-partial wetting. Both S and A are positive.

1.2.5 Pseudo-partial wetting

This wetting is characterized by a positive spreading parameter S and a positive Hamaker constant A .

Depending on the particular shape of $\Pi(h)$, sketched in Figure 1.6, Brochard-Wyart predicted another type of wetting designed as pseudo-partial wetting, for which the interaction between the solid and the non-wetting phase (usually vapor) is attractive at long range and repulsive at short distances. In this situation, a macroscopic equilibrium contact angle θ_e coexists with a thin wetting film of thickness h_e , sketched in Figure 1.7, which is a result of the long-range interaction forces. θ_e and h_e are related in equilibrium, but depend on the considered conditions (fixed volume, fixed pressure, size of the droplet ...) [30]. The free energy presents a minimum at a thickness of film h_m in Figure 1.6, which corresponds the final equilibrium state of this droplet with a spherical cap and a film of thickness h_m . The contact angle θ in equilibrium is given by a balance of forces acting on the contact line:

$$\gamma_e = \gamma \cos \theta \quad (1.11)$$

where $\gamma_e = \gamma + h\Pi + P$ is the effective interfacial tension of the microscopic film. For $h = h_m$, $\Pi = 0$ and $\gamma_e = \gamma + P$.

We will present an example of spherical droplet under this wetting and some experimental results in Chapter 3. We will also present that this wetting is common under a liquid/liquid/solid system, when the substrate is grafted by a layer of silane. But to well understand this wetting, we should distinguish pseudo-partial wetting from precursor

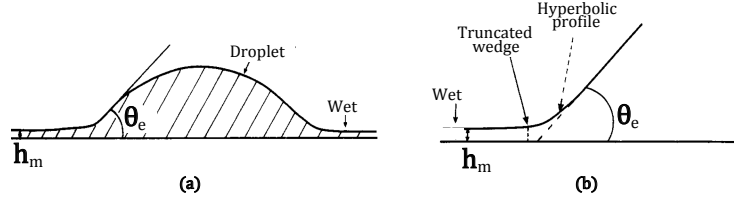


Figure 1.7: In pseudo-partial wetting condition, the final equilibrium state of a large droplet (a) and its wedge profile (b). There is a spherical cap and a film of thickness h_m corresponding to the minimum of $F(h)$ shown in Figure 1.6. The droplet and the film join with a hyperbolic profile. The truncated wedge is discussed by Wayner [29].

film under complete wetting in section 1.2.5.1 and frustrated complete wetting in section 1.2.5.2.

1.2.5.1 Precursor films

Under complete wetting situation, for S at the order of γ , during the spreading of a droplet, the van der Waals forces lead to the formation of a precursor film in front of the contact line. Precursor films should be distinguished from films that exist in equilibrium, and help us to understand the dynamical film structure that precedes a spreading drop [31]. Away from the liquid drop, the thickness of precursor film is typically just a single molecular layer.

These films are established by flow from the main drop. This feature was confirmed by using ellipsometry [32, 33], interference patterns [32], polarized reflection microscopy [34], and phase-modulated interference microscopy [35].

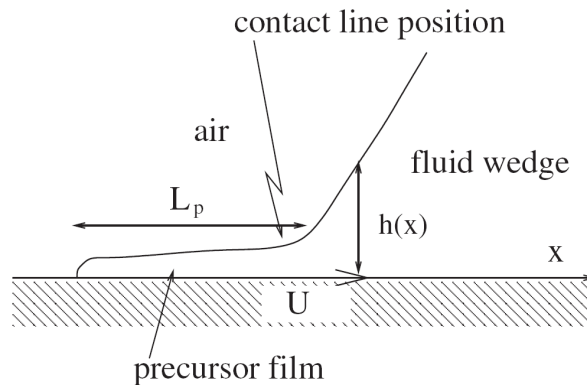


Figure 1.8: Schematic drawing of a moving contact line for complete wetting $S > 0$, $A < 0$. Ahead of the apparent contact line there is a precursor film driven by van der Waals forces.

1.2.5.2 Frustrated complete wetting

We should discuss about another intermediate wetting state, called frustrated complete wetting, which is characterized by a mesoscopic wetting film [36]. As only the long-range interactions oppose to the formation of a macroscopic wetting film [37]. With $A > 0$, the Van der Waals interactions generate an attractive force between the two interfaces. This force promotes the gas phase to contact the substrate, and the short-range interactions promote the liquid phase on the surface. So the short and long-range interactions have contrary effects.

While, in the situation with a mesoscopic wetting film, the long-range interactions oppose the complete wetting of liquid phase and tend to diminish the wetting film, the short-range interactions tend to promote the wetting of gas phase with the substrate, and induce the wetting transition, frustrated complete wetting [38, 39].

In the thesis work of Bertrand [16], he distinguished pseudo-partial wetting from frustrated complete wetting. For pseudo-partial wetting the thickness of microscopic film is determined by the competition between the short-range interactions, which promote the spreading of droplet, and the positive Hamaker constant, which tends to diminish the wetting film. For the frustrated complete wetting, the interfacial potential of short-range interactions is negligible. The thickness of mesoscopic film is determined by the equilibrium between Hamaker constant, which promotes the microscopic wetting film, and the second term of development of interfacial potential of Van der Waals, which promotes a macroscopic film.

We treat the pseudo-partial wetting and frustrated complete wetting as the same. Because the appearance of macroscopic drop and microscopic wetting film around it give the same criteria. And the same shape of disjoining pressure needs a system with a minimum free energy with a infinite thickness.

From an experimental point of view, pseudo-partial wetting has been observed with a rather limited number of systems the wetting of air/pentane/water [40] by neutron reflectometry [41], of air/alkane/brine-AOT by ellipticity measurements [42–44], and of air/PDMS/surfactant solution by a video microscope [45, 46]. Despite this few examples, this type of wetting has inspired several theoretical works that focused on the shape of interface from the macroscopic scale to the microscopic one [30, 47, 48].

Bertrand [16] reported temperature-induced wetting transitions for different alkanes and a novel pressure-induced wetting transition for an alkane mixture. The experiments enable us to determine the global wetting phase diagram as a function of chain length and temperature which they subsequently calculate theoretically, as shown in Figure 1.9. The two transition lines are found to be approximately parallel, in accordance with basic theoretical arguments [37].

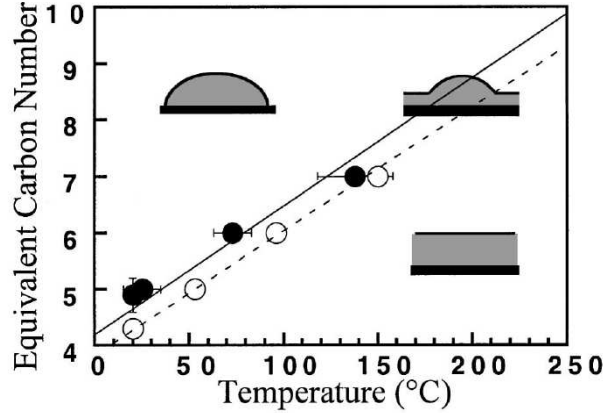


Figure 1.9: Wetting phase diagram as a function of chain length and temperature: the filled circles correspond to the experimental wetting transitions and the solid line is the theoretically calculated line. The open circles correspond to the experimental critical wetting transitions and the dashed line is the theoretically calculated critical wetting transition line [37].

1.3 Shape of the interface and equilibrium properties

In the previous section, we described the different wetting situations. Here our aim is to describe the shape of the interface between the fluids and the solid in the absence of gravity. We will consider two geometrical situations : the plate and plate geometry and geometries displaying wedges. We will suppose that Bond numbers are small, and neglect gravitational effects. We will then discuss the shape of the interfaces in those geometry as a function of the wetting situation.

1.3.1 Plate and plate geometry

We first deal with the plate and plate geometry, which is equivalent, up to a factor of 2, to the case of a circular tube. We consider two infinite plates separated by a distance h , as sketched in Figure 1.10. The geometry is loaded by two fluids (fluid 1 and fluid 2) and we wonder what is the shape of the interface. We note P_0 and P as the pressures, respectively in fluid 1 and fluid 2.

1.3.1.1 Partial wetting situation

We first consider the partial wetting situation. At rest, there is no flow. The pressure field are homogeneous and the pressure gradient sets the shape of the interface:

$$P_0 - P = \gamma \left(\frac{1}{R_a} + \frac{1}{R_b} \right) \quad (1.12)$$

where R_a and R_b are the two curvature radii of the interface.

This equation is supplemented by boundary conditions that set the contact angle at the solid interface. Following Eq:1.9 the contact angle on a perfect substrate at equilibrium is given by the knowledge of spreading parameter S . We recall that $S = \gamma_{S1} - (\gamma_{S2} + \gamma_{12}) = \gamma_{12}(\cos\theta_e - 1)$.

In the partial wetting case, the interface is thus of small area and there does not exist microscopic films. For an ordinary (disordered) substrate, the situation is more complex. The surface has chemical defects (its chemical compositions vary from point to point) or physical defects (surface roughness). Contact angle of sessile drop θ_e on this kind of surface is not unique. If we inject more liquid into this drop through a needle, the drop remains pinned to its contact line and its contact angle increases until a threshold value, often noted advancing contact angle θ_a , beyond which the contact line advances. Reciprocally, if we decrease its volume by pumping the liquid, its contact line remains pinned until another threshold value θ_r , the receding contact angle. Classical point of view about hysteresis describes that triple line is pinned and immobile whenever θ lies within a finite interval $\theta_r < \theta_e < \theta_a$ [13]. We could define the hysteresis of contact angle:

$$\Delta\theta = \theta_a - \theta_r \quad (1.13)$$

An ideal solid surface is flat, rigid, perfectly smooth, chemically homogeneous, and has zero contact angle hysteresis. Practically, a good surface could be defined by a small hysteresis $\Delta\theta \leq 5^\circ$. If we place a droplet on a non-cleaned glass, the hysteresis $\Delta\theta$ could be several dozen degrees, which has been studied by Johnson and Dettre on substrates with various roughness [49].

We still have a poor understanding of the hysteresis for random substrates as we have no theoretical or experimental answer to such basic questions as how hysteresis depends on the density of defects or on the strength of the defects.

1.3.1.2 Pseudo-partial and complete wetting situation

The shape of the interface between the two liquids is more complex. Microscopic films may exist.

We consider a film of thickness h_e , in equilibrium with a meniscus inside a flat tube of radius R (see Figure 1.10). There is a macroscopic contact angle, provided that disjoining pressure $\Pi(h)$ is negative at long range, as sketched in Figure 1.11 or Figure 1.6.

Derjaguin's equation (Equation 1.4) applies to determine the shape of the meniscus and reads in two dimensions [24]:

$$p_0 - p(x) = \gamma \frac{h_{xx}}{(1 + h_x^2)^{3/2}} + \Pi(h) \quad (1.14)$$

In the macroscopic meniscus, the disjoining pressure could be neglected, and the previous equation leads to constant curvature, so that the macroscopic contact angle is linked to the pressure difference by $p_0 - p = 2\gamma \cos\theta/R$. Far from the meniscus (towards the h_e

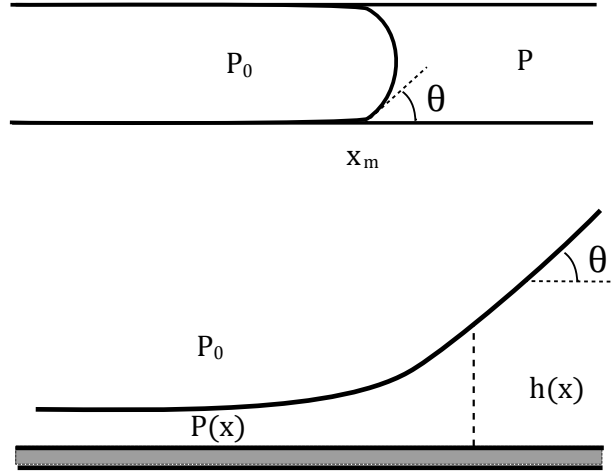


Figure 1.10: Schematic drawing of the considered situation: a meniscus in a tube, where the pressure of the two phases are p_0 and p . Below: a zoom on the contact line region showing the intermediate region between the macroscopic meniscus and the thin wetting film.

decreasing direction), the thickness h_e of the wetting film is given by $p_0 - p = \Pi(h)$. For θ smaller than $\pi/2$, integration of Equation 1.14 leads to:

$$(p_0 - p)(R - h_e) = \gamma + \int_{h_e}^R \Pi(h)dh \quad (1.15)$$

which gives after usual approximations an additional relation between the macroscopic contact angle and the disjoining pressure:

$$2 \cos \theta = 1 + \frac{1}{\gamma} \int_{h_e}^{\infty} \Pi(h)dh \quad (1.16)$$

This shape of disjoining pressure thus allows the coexistence between a macroscopic contact angle θ and a film of thickness h_e . Note that h_e is always higher than a thickness h_{min} , solution of $2\gamma/R = \Pi(h)$, and should also be smaller than h_{max} . However, considering in more details stability criteria and following Starov [18] [Wetting and spreading dynamics], a solution with $\theta > \pi/2$ is not stable.

At equilibrium, the pressure is uniform inside both phases and thus $2\gamma \cos \theta_e / R = \Pi(h_e)$. Then, Equation 1.16 is the integration of the generalized Laplace law from the meniscus region to the flat wetting films, which constitutes the second equation needed to define the equilibrium state [18]. Thus there is only one equilibrium contact angle expected for pseudo-partial wetting systems with ideal surfaces. In the complete wetting situation, the macroscopic angle is equal to $180^\circ C$. The thickness of the film is set by the disjoining pressure $\Pi(h)$.

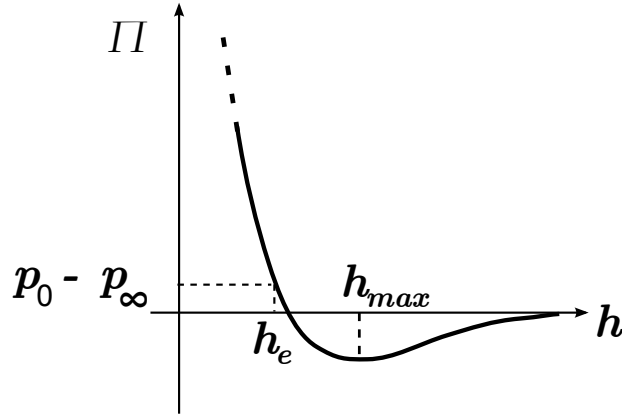


Figure 1.11: Schematic drawing of the disjoining pressure under consideration. Interactions are attractive at long range, and repulsive at short distance, so that there exists a stable film whose thickness is below h_{max} .

1.3.2 Existence of corner films

The shape of the interface between two liquids may differ in complex geometries. The presence of wedge has some important consequences on the equilibrium shape of the interfaces, due to capillarity. Indeed, the combination of a uniform curvature of the interface and the boundary conditions of fixed angle at the solid surface leads to the formation of an long liquid rivulet along the wedge, providing that the opening angle of the wedge is low enough. The existence condition of such a stable rivulet in a wedge of opening angle α is given by the Concus-Finn relation [50], which reads

$$\theta < \pi/2 - \frac{\alpha}{2}, \quad (1.17)$$

where θ is the contact angle.

In order to understand this relation, let us consider a tube that have a circular cross section except in one edge such as the schematic drawing in Figure 1.10, the curvature between the two phases is given by $2 \cos \theta / R$, where R is the tube radius. Far from the meniscus, we expect for an infinite rivulet that the curvature has only one dimension. The cross-section of the rivulet is schematic drawingd in Figure 1.12, which defines the notations used. Its curvature is given by $\cos(\theta + \alpha/2) / l \sin(\alpha/2)$. The size l of the rivulet is thus given by

$$l = R \frac{\cos(\theta + \frac{\alpha}{2})}{2 \cos \theta \sin \frac{\alpha}{2}} \quad (1.18)$$

From this equation, one recovers directly the Concus-Finn relation, by stating that l is necessary positive. Here it has been implicitly assumed that $\theta < \pi/2$, that is to say we have considered the fluids that preferentially wets the solid surfaces. The problem is of course symmetric.

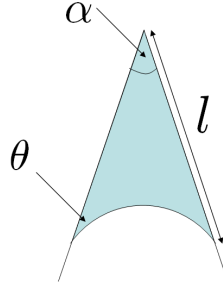


Figure 1.12: Schematic drawing of non-circular tube exhibiting a wedge of angle α .

It is interesting to focus on the particular case of $\alpha = \pi/2$, which will be the situation encountered experimentally in tubes of square cross-sections. Then, the size l of the corner film is given by $R(\cos \theta - \sin \theta)/2$. There exists corner films only for $\theta < \pi/4$. In the limit of small contact angles, the size l is one fourth of the channel size.

Note that those considerations are valid for all the wetting situations. The angle involved in the Equation.1.18 is the contact angle in the partial wetting situation, the macroscopic contact angle in the pseudo-partial wetting situation and Π in the complete wetting situation.

From a practical point of view, these corners are very often present in porous media because of the complex geometry.

1.4 Wetting dynamics

In the previous section, we have described the features of the wetting in equilibrium. In this section we deal with wetting dynamics. Despite much research over many years, the precise mechanism, by which a liquid front advances on a solid remains only partially understood. The main parameters used to quantify the wetting dynamics are the relative velocity and the dynamic contact angle θ_d . The first one is a velocity at which the liquid moves across the solid, *i.e.* the wetting-line velocity V . The second one may be an angle, which is formed between the moving liquid interface and the solid surface at the line of three-phase contact (the contact line). The dynamic contact angle is the key boundary condition. The relation between the velocity and the angle depends upon the presence or absence of wetting films and thus upon the nature of the wetting. However, little is known concerning the dynamics properties of wetting and spreading in pseudo-partial wetting situation. Since it is an intermediate situation between partial wetting, where contact angle hysteresis plays an important role at low velocities, and complete wetting, where there is no hysteresis, the description of the dynamics under pseudo-partial wetting asks for experimental studies. In the following we will describe the partial, pseudo-partial and complete wetting situation. We will not discuss the existence of corner films. Even though their roles have been pointed out in the literature, a comprehensive description of the flow

in those films has not yet been given.

1.4.1 Wetting dynamics: partial wetting situation

This section deals with the wetting dynamics in the partial situation case. Several attempts have been made in the literature to explain the observed behaviors. At this stage, three main approaches are used. They differ from each other both in terms of their conceptual frameworks and in their identifications of the effective channels of energy dissipation.

The first one introduced by Cox is a hydrodynamic approach. The dissipation is due to the viscous flow within the wedge of the liquid near the moving contact line. Changes in the experimentally observed (and therefore macroscopic) dynamic contact angle are attributed to the viscous bending of the liquid-gas interface within a mesoscopic region below the scale of observation.

The second approach originates from the Frenkel/Eyring view [51] of liquid transport as a stress-modified molecular rate process. This approach discards dissipation due to the viscous flow. It focuses instead on what occurs in the immediate vicinity of the moving contact line due to the process of attachment or detachment of fluid particles (molecules) to or from the solid surface. The last approach is more recent and is formally similar to the second one. It is however conceptually very different since the thermally activated process concerns successive pinning and depinning of the contact line.

1.4.1.1 Hydrodynamics approach

Following the hydrodynamic approach, changes of the dynamic contact angle are observed experimentally (and therefore macroscopically). These changes are attributed to viscous bending of the liquid-gas interface within a mesoscopic region below the scale of observation. The microscopic contact angle θ_m is usually assumed to be governed by short-range intermolecular forces and to retain its static value θ_e , though empirical relationships between θ_m and V have also been proposed as a way of specifying θ_m . Within this hydrodynamic model there are therefore three relevant length scales, as shown in Figure 1.13.

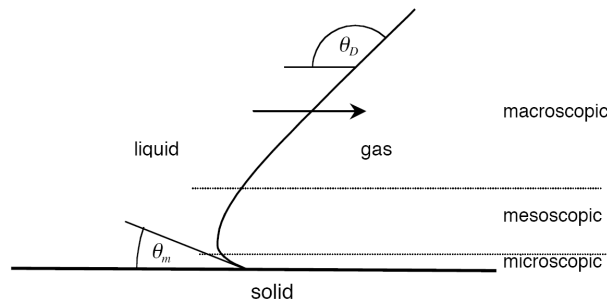


Figure 1.13: Schematic representation of viscous bending on the mesoscale for an advancing meniscus. There are three relevant length scales [52].

As it is well known, the classical hydrodynamic approach, which describes the flow near a moving wetting line, does not result in a physically acceptable solution. Because of the conflict between a moving contact line and the conventional no-slip boundary condition between a liquid and a solid, stresses are unbounded at the wetting line. The force exerted by the liquid on the solid becomes infinite. One approach to deal with this singularity has been to truncate the solution artificially at the molecular scale where the continuum description breaks down. Alternatively, the flow equations and boundary conditions have been modified by relaxing the no-slip condition in the vicinity of the contact line. In this case, the force exerted on the solid is then finite, though the stresses in the liquid remain unbounded. The balance between the energy dissipation and the interfacial tension energy leads to a relation, which describes the change in the dynamic contact angle due to viscous bending of the liquid-gas interface. For low dynamic contact angle ($\theta_d < 3\pi/4$), it may be written in terms of the capillary number as:

$$\theta_d^3 - \theta_m^3 = 9Ca \ln(L/l_m) \quad (1.19)$$

where $\ln(L/l_m)$ is a fitting parameter. L and l_m are appropriately chosen macroscopic and microscopic length scales, respectively. This is noted as Cox-Voinov's Law.

If the hydrodynamic model is applied to the spreading of small drops and small contact angles, Equation 1.19 leads to simple scaling laws for the base radius R and the dynamic contact angle θ_d as a function of time t . It is the Tanner law (see Equation 1.24 and 1.25). These relationships have been widely confirmed for small drops of completely wetting liquids [53–56]. This result is sometimes advanced as a more general demonstration of the validity of Equation 1.19 and its underlying assumptions.

1.4.1.2 Molecular-kinetic theory

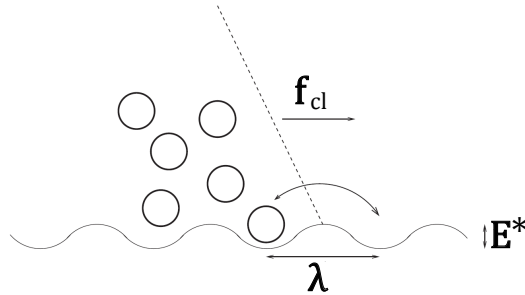


Figure 1.14: Schematic drawing of the molecular-kinetic theory by Blake and Haynes [57]. Contact line motion is the hopping of molecules between the potential wells provided by the substrate.

A few years before the emergence of the various derivations of the hydrodynamic theory, Blake and Haynes proposed a rather different approach to describe the contact line movement. It supposes that the microscopic processes, that take place in the vicinity of the

contact line, dominate the dissipation, in contrast to the hydrodynamic approach, where this contribution is neglected (the microscope scale is even truncated in the integration). In the original "molecular-kinetic model" [57, 58], shown in Figure 1.14, the dynamics of the contact line is a result of jumps at the molecular scale from one adsorption site to another. The thermally activated process is controlled by two parameters: the microscopic size λ of elementary activated jumps and E^* , an "activation free energy of wetting" [57].

E^*/λ^2 is expected to be in the order of the energy of adhesion between solid and liquid.

The idea is that under a force f_{cl} at the contact line, each individual molecules jump over a length λ in a local minimum of energy of depth E^* . At thermal equilibrium, backward and forward jumps are equal. The applied forces per molecule $f_{cl}\lambda$ deforms the potential landscape to make forward steps, so that the frequency $1/\tau$ of these jumps is given by

$$\frac{1}{\tau} = \frac{2}{\tau_0} e^{-\frac{E^*}{k_B T}} \sinh \frac{\lambda^2 f_{cl}}{2k_B T} \quad (1.20)$$

where τ_0 is a microscopic time for a single "attempt". Since the contact line speed is $V = \lambda/\tau$, one thus obtains

$$V = \lambda \nu_0 e^{-\frac{E^*}{k_B T}} \sinh \frac{\lambda^2 \gamma (\cos \theta_e - \cos \theta_d)}{2k_B T} \quad (1.21)$$

where ν_0 is a thermal frequency ($\nu_0 \approx k_B T/h$).

This equation is generally used in its linearized form since λ is a molecular size and the argument of the hyperbolic sine is smaller than 1. In this limit, the various unknown parameters reduce to a single one. If λ has a clear physical meaning, the energy E^* is less clear. Pomeau [59] proposed that E^* is estimated as the heat of evaporation per molecule, which would lead to $e^{E^*/k_B T} \approx \rho_{liquid}/\rho_{gas} \approx 10^3$, significantly enhancing the speed dependence of the microscopic contact angle. Recently, it was also proposed that E^*/λ^2 is in the order of the work of adhesion $W_A = \gamma(1 + \cos \theta_{eq})$ [60]. However, these are order-of-magnitude estimates, and given the very strong dependency of the contact line velocity with respect to λ and E^* , effectively one has to treat $\lambda^3 \nu_0 \exp((-E^*/k_B T)/2k_B T)$ as an adjustable parameter, to infer the dynamic contact angle θ_d .

1.4.1.3 Combined model

Despite their fundamentally different physics and somewhat different predictions, both the hydrodynamic and molecular-kinetic models have been shown to be reasonably effective in describing the experimentally observed behavior of the dynamic contact angle in a range of systems. While hydrodynamic approach predicts that for small contact angles $V \propto \theta^3$, molecular-kinetic theory predicts $V \propto \theta^2$.

In the past, opinion regarding the two models has appeared somewhat polarized. However, a point of view that is gaining increasing ground is the possibility that both wetting line friction and viscous dissipation play a part in determining the dynamic contact angle. Leaving aside the specific details of the two models, it seems self-evident, on simple thermodynamic grounds, that the microscopic contact angle will be disturbed by movement of

the contact line, and equally self-evident that viscous flow in the small wedge of liquid near the contact line is likely to modify the meniscus profile in this region. The real question concerns the relative importance of the two effects and how they can best be described.

Considering dynamic wetting as an irreversible process, Brochard and de Gennes [61] assume that the rate of energy dissipation per unit length of the wetting line is the product of the flux U and the out-of-balance interfacial tension force $\gamma(\cos(\theta_e) - \cos(\theta_d))$. If one then supposes that the total energy dissipation comprises the viscous losses in the (thin) wedge of liquid adjacent to the moving wetting line plus the losses due to wetting-line friction, then, using simplified arguments, one obtains:

$$\gamma(\cos(\theta_e) - \cos(\theta_d))V = \frac{6\eta V}{\theta_d} \ln(L/L_m)V + \xi V^2 \quad (1.22)$$

Here, the lengths L and L_m together with the contact angle θ_d define the wedge of liquid in which viscous dissipation occurs (estimated using the lubrication approximation). The length L characterizes the size of the wedge, and L_m the molecular limit where continuum mechanics breaks down. Because the contact angle of the wedge θ_d occurs in the denominator of the viscous term, viscous dissipation dominates at small contact angles. Brochard-Wyart and de Gennes interpreted the friction coefficient ξ in terms of the molecular-kinetic theory.

Others similar expression have been obtained by Petrov [62,63] and de Ruijter [64].

1.4.1.4 The Shikhmurzaev model

A natural starting point for the modeling is the definition of a contact angle through the equation which introduces this concept into macroscopic fluid mechanics. On a macroscopic length scale, the interfaces are modeled as geometrical surfaces of zero thickness possessing some specific "surface" properties, first of all the interfacial tension. When the liquid is at rest, the static contact angle θ_e is introduced through the well-known Young's equation, which from a mechanical standpoint is simply the projection of the force balance on the tangent to the solid surface assumed to be smooth and chemically homogeneous. When the contact line is moving, the force balance equation remains valid, but the fact that θ_d changes suggests that at least one value of the interfacial tension is changing. Shikhmurzaev [65] suggests that this change comes from temporal transient and from the requirement for a fluid particle to adapt its properties to its neighborhood. Indeed, if we look at the flow in the reference frame moving with the contact line, we will see that a fluid element, which initially belongs to the free surface, arrives at the three-phase interaction region, traverses it in a finite time to become an element of the liquid-solid interface, and is finally driven away from the contact line by the moving solid wall. Hence, the interfacial tension and other surface properties associated with this fluid element have to change from values corresponding to the liquid-gas interface to those of the liquid-solid interface. This process, which is of course not instantaneous, gives rise to a interfacial tension gradient in the vicinity of the contact line. The shear-stress singularity is removed since the interface

and the solid have their own velocity in this model. Note that no slip between the liquid and the solid is assumed.

This leads to :

$$\cos(\theta_e) - \cos(\theta_d) = \frac{2V(\rho_{2e}^s + \rho_{1e}^s u_0(\theta_d))(1 - \rho_{1e}^s)^{-1}}{(V^2 + \rho_{2e}^s)^{1/2} + V} \quad (1.23)$$

where V is the nondimensional contact line velocity, $u_0(\theta_d)$ is the tangential component of the free surface velocity in the reference frame moving with the contact line, ρ_{1e}^s and ρ_{2e}^s are equilibrium surface density corresponding to the liquid-gas and liquid-liquid interface.

1.4.1.5 Comparison with experiments

In this section, we examine the success of the models outlined before. Comparison between experimental data and theoretical model is a difficult task. In dynamic contact angle experiments, it is clearly important to measure the angle as accurately as possible over the widest possible range of wetting line speeds and angles. Unless this is done, it is difficult to assess which theory is effective or not.

We will see in the following examples that at this stage it is difficult to clearly define which theory applies to which wetting situation. Hoffman's data [66] deals with silicone oils in a glass capillary. Silicone oils wet clean glass, so a precursor film is probable. Both the conventional hydrodynamic theory and the molecular kinetic theory are able to represent the data reasonably well, with sensible values of the fitting parameters. We note that the fit with the hydrodynamic model is slightly better. Note that the fit has to be truncated to $\theta_d < 3\pi/4$ due to the expansion made in the calculation.

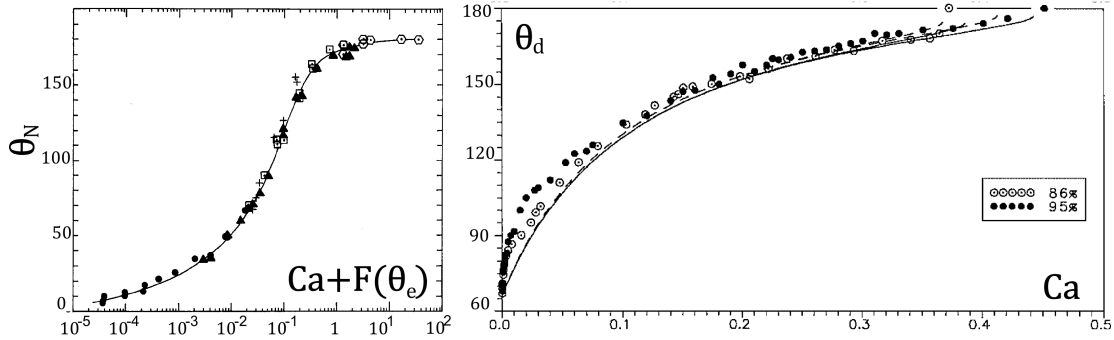


Figure 1.15: Effect of flow on apparant contact angle of an advancing liquid-air interface.

Blake *et al* [67] studied the contact angle for a polyethelene terehtalate (PET) tape plunging into a pool of aqueous glycerol mixture. For Ca less than 1×10^{-3} , only the molecular kinetic theory provides a good fit to the data. For high values of Ca both theory describe the data. We note that the parameter used to fit the data at low speed are not consistent with the one used at high speed when the molecular kinetic theory is used. Same contradictions were observed by G.N. Batts using di-n-butyl phthalate on PET at $55^\circ C$

(*Kodak Limited R & D*) [52]. This suggests that both channels of dissipation play a role in the displacement of the triple line. Hydrodynamics seems to play the major role for high value of the capillary number whereas molecular displacement are in charge of what happens at small viscosity. Overall it seems that neither model is universally applicable but that both hydrodynamic and molecular mechanisms are at work: that viscous bending may occur, but θ_m is also speed dependent. Combined model is thus a way to describe the entire curve. This is specially true if the data is restricted to a narrow class of liquids.

An exception is in the case where one viscous liquid displaces another. Here serious discrepancies have been found experimentally with the hydrodynamic model whether the molecular-kinetic model describes well the data [68]. Note that applying Shikahmurzaev's model may in some case give a good precision even though some discrepancies may be found for low capillary number.

At this stage, no clear model emerges and experiments dealing with a wide range of liquids are required to probe these theories. More importantly for a practical point of view, none of these theory deals with the contact angle hysteresis, which is one of the most important features that need to be taken into account at low capillary numbers. In all the approach, the equilibrium contact angle is taken to be either the advancing one, either the receding one, depending on the contact line motion.

1.4.1.6 Thermally activated depinning theory

The last approach which has emerged more recently is based on a thermally activated motion, similarly to the molecular kinetics theory (MKT). However, the physical mechanism of the motion is rather different. Instead of molecular jumps, Prevost *et al.* proposed, that, on a disordered substrate, the thermally activated jump corresponds to successive depinning events from one defect to another [19, 69]. The idea of this model, designed thereafter as the "thermally activated depinning theory" is that for the contact line to move under a force $f_{cl} = \gamma(\cos\theta_e - \cos\theta_d)$, per unit length on the contact line, the contact line has to unpin the mesoscopic pinning sites of the surfaces [19, 70].

Although this model is formally equivalent to the MKT and leads to the same equation (see Equation 1.21), λ and E^* have a very different physical meaning. λ is now the correlation length of the disorder and E^* the typical energy barrier between two pinned configurations of the contact line. The corresponding orders of magnitude are thus very different, and, consequently, the Equation 1.21 could no more be linearized. Indeed, the argument of the hyperbolic sine is now larger than 1 and the dynamics is exponential. Similarly to the MKT, the additional viscous dissipation considered in the hydrodynamic theory should be added to the model to be able to describe high- Ca regimes.

Taking advantage of the very low viscosity of supercooled helium system, Prevost *et al.* reported a set of measurement, that strongly indicates in this case such a model applies. Since the superfluid helium-4 does not wet cesium at low temperature [71], it makes viscous dissipation negligible below 2.17 K. This system has been proven useful to study some of general features of wetting transition such as the roughness of contact line on a disordered substrate [69]. Prevost *et al.* have measured the contact angle of

a liquid helium-4 meniscus on a cesium substrate as a function of velocity of the three phase contact line at low temperature. Equation 1.21 gives the exponential dependence of velocity V and dynamic contact angle $\cos\theta_d - \cos\theta_e$ in Figure 1.16 for sufficiently large forcing $f_{cl}\lambda^2/k_BT \gg 1$. The dynamics is indeed found to be exponential with respect to the driving force and thermally activated (see Figure 1.16). Since both f_{cl} and k_BT are known experimentally, the fits of Figure 1.16 determine the activation length λ . For the helium system under study, $\lambda \cong 15$ nm is found, which is significantly larger than any atomic distance and which matches the surface correlation length of the defects.

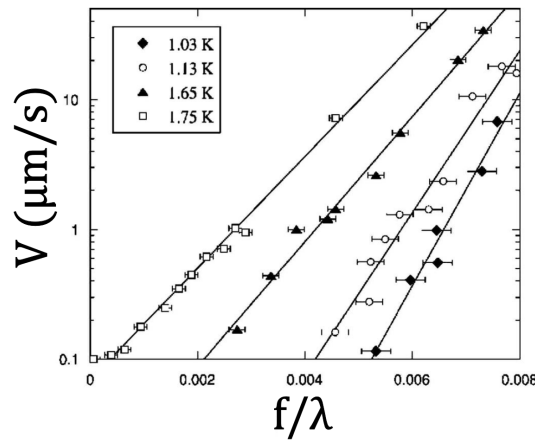


Figure 1.16: Contact line velocity plotted as a function of the applied forces per unit length f_{cl} for various temperatures under a liquid helium-4/cesium substrate system [70]. Solid lines are exponential fits to the experimental data.

This approach has been followed by Petrovet *et al.* [62,63], to obtain E^* and λ for a range of low viscosity alcohols on an amorphous substrate. Remarkably, the length λ is found to be in the order of 8 nm, in qualitative agreement with the activation length extracted from Figure 1.16. This result once again points to a process, which limits the contact line velocity and takes place on scales much larger than a molecular length. It has been suggested by Prevost *et al.* that λ is to be identified with the density of pinning sites, at least for the systems mentioned above.

Up to our knowledge, rather few experiments have been yet reported to validate this third approach.

1.4.1.7 Thermally activated depinning theory and Hysteresis

One of the main success of the thermally activated depinning theory is to be able to describe the contact angle hysteresis as well as the dynamics at low capillary numbers. Recalling that the hyperbolic sine is not in its linear range in the case of high λ , the velocity predicted by this approach naturally exhibits many order of magnitudes and an apparent "pinned" regime where the velocity is very low, corresponding to the macroscopic

contact angle hysteresis. The activated regime is nothing but a thermal rounding of the depinning transition.

Disorder leads to contact line pinning, which in turn provokes the hysteresis of contact line. The precise value of the threshold is not universal: it depends on the shape and density of the defects, their chemical nature, etc.

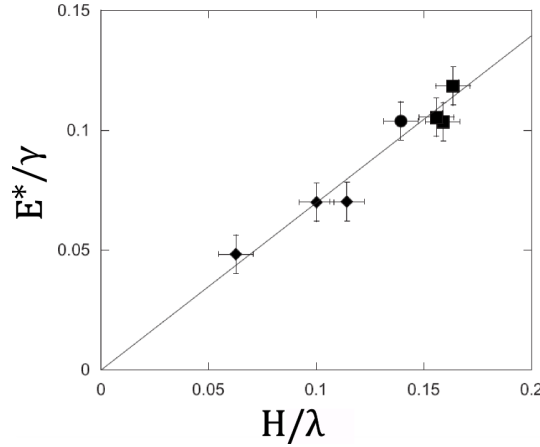


Figure 1.17: Activation energy as a function of the hysteresis for liquid hydrogen on various disordered cesium substrates.

In the depinning approach, there is a single physical mechanism and a single energy scale E^* , which controls both the dynamics close to the threshold and the hysteresis H . Such a simple picture makes sense for systems such as cryogenic liquids on alkali-metal substrates. For such substrates with a disorder scale in the order of 10 nm, Rolley and Guthmann [19] showed that E^* is in the order of H , as sketched in Figure 1.17. Measured values of E^* are on the order of hundred $k_B T$. A clear prediction of these energy is however still lacking at present.

In summary, it seems that the motion of a contact line is still an open question, as reflected by the three groups of theories presented above. If the thermally activated depinning theory that is emerging is appealing since it allows one to describe the contact angle hysteresis, it suffers up to now of a lack of experimental validation and needs an additional approach to describe the dynamics at higher Ca , at least when viscous dissipation could not be neglected.

1.4.2 Wetting dynamics: complete and pseudo-partial wetting situation

The presence of wetting films modifies the wetting dynamics. In this section, we address this question. We have decided to group complete and pseudo-partial wetting situation since they only differ by the A value. At small scale, they display repulsive interactions that

create a wetting film. Scriven has exposed this subject at length in [72]. In the following we will present the major points and the major conclusion of this article. The prototype flow considered here is relevant to the displacement of a fluid by another between two plates. A numerical result, which is calculated by Dr. Hugues Bodiguel, is also presented. As in the previous section, corners films are absent in this situation.

1.4.2.1 Wetting films under complete wetting

The spreading of a complete liquid has been well discussed in literature. We recall the main results in three situations.

Spreading of a droplet A droplet spreads and achieves a thin wetting film on a smooth homogeneous substrate. Its thickness is answered by Tanner [53]. During the spreading, the drop radius has a power law with time:

$$R(t) \approx \left[\frac{10\gamma}{9B\eta} A \right]^{1/10} \propto t^{1/10} \quad (1.24)$$

designed as Tanner law. The constant B is estimated theoretically: $B^{1/10} = 1.186$, and A is a constant: $A = (4V/\pi)^3$. The power $1/10$ found for the viscous spreading of small droplets has been well corroborated by many other experiments [54–56]. Tanner law could be also written for the dynamic contact angle and reads:

$$\theta_d \approx t^{-3/10} \quad (1.25)$$

Wetting film on a solid plate When an infinite plate is withdrawn (at an angle α to the horizontal, with a constant velocity V) from an infinite pool of viscous liquid under complete wetting situation. A layer of liquid film is therefore deposited on the plate surface. Landau, Levich and Derjaguin [73,74] proposed a model (LLD model) to describe this thickness under the form:

$$h \approx \kappa^{-1} Ca^{2/3} \quad (1.26)$$

which describe the evolution of this deposited wetting film, $\kappa^{-1} = 0.95$. This validity condition is given as $l \ll Ca$.

Wetting film in a capillary tube In a circular tube with radius b , which is much smaller than the length l . The thickness of wetting film is given by Bretherton law [75]:

$$h \approx b Ca^{2/3} \quad (1.27)$$

which describe the thickness of deposited wetting film in a circular tube.

This law is not valid if the radius of tube is big, $h \ll b$. In this situation, we need to consider a geometric correction [76]. As Bretherton law initially describes the displacement of bubble in water, it is not necessary to consider the viscosity ratio. But in the situation

with liquid/liquid meniscus, Scharz *et al* demonstrated that Bretherton's law stays valid with a rather small change of the prefactor, which depend on the viscosity ratio, provided that Ca here is defined with displaced fluid [77].

1.4.2.2 Theory of forced displacement

A meniscus between two immiscible phases advancing between two plates leaves behind him a film of the fluid, which is displaced. Provided the displacement speed measured by the capillary number is small ($Ca = \eta V / \gamma < 0.01$), the leading portion of the meniscus is dominated by capillarity and is thus in good approximation described by a static meniscus. Behind the film displays a uniform thickness. A transition zone connects the two regions. The equation governing the shape of the film relies on a balance of viscous capillary and disjoining forces and momentum fluxes acting on a slice of a film of differential thickness in the main direction of the flow.

$$0 = (H-h) \frac{\delta \gamma_{sf}}{\delta x} + (H-h) h \frac{\delta}{\delta x} (2K) \gamma_{ff} - h (\tau_{xy}^{(1)}(x, H) - (\tau_{xy}^{(1)}(x, h)) + (H-h) (\tau_{xy}^{(2)}(x, h) - (\tau_{xy}^{(2)}(x, 0))) \quad (1.28)$$

where γ_{sf} is the solid-film tension due to intermolecular forces, $2K$ is twice the mean curvature of the fluid-fluid interface, γ_{ff} is the fluid interfacial tension and τ_{xy} is the shear component of the viscous stress tensor. The superscripts 1 and 2 denote the displacing and displaced fluids, respectively.

$\delta \gamma_{sf} / \delta x$ can be expressed in terms of the disjoining pressure. It is equal to

$$\frac{\delta \gamma_{sf}}{\delta x} = h \frac{\delta \Pi}{\delta h} \frac{\delta h}{\delta x} \quad (1.29)$$

The continuity of the fluid velocity and of the shear stress at the interface allow us to find the film profile equation in the low-slope approximation.

$$\frac{d}{dx} \left[\frac{h_{xx}}{(1 + h_x^2)^{3/2}} \right] = - \frac{H^2}{\gamma_{ff}} \frac{\delta \Pi}{\delta h} h_x + 12 Ca (h - h_\infty) \frac{G(h)}{(4(1-h)^2 + 3mh(1-h))h^3} \quad (1.30)$$

$$G(h) = (1-h)^2 + m \left[\frac{(3-h_\infty)(h+h_\infty) + (3m-2)h_\infty h}{2(1-h_\infty)^2 + 3mh_\infty(2-h_\infty)} - h^2 \right] \quad (1.31)$$

where Ca is the capillary number.

In absence of displacement, at rest we get the augmented Young-Laplace equation (see Eq 1.16). This equation links the contact angle to the disjoining pressure and the film thickness.

1.4.2.3 Contact line profile in displacement

In the displacement situation, solving the previous set of equation requires numerical simulation or numerical expansions. The results distinguish two regimes of capillary number for two dimensional steady displacements. At low capillary number, displacements can be

classified as quasi static. In this regime, the film profile is governed almost entirely by capillarity and disjoining pressure: meniscus shape is given in good approximation by the augmented Young Laplace equation. At higher capillary pressure, wetting properties, as determined by disjoining pressure, are insignificant and Bretherton's purely hydrodynamic theory governs the shape of the film. The transition between the two regimes is abrupt extended over no more than an order of magnitude of capillary number. We have analyzed in great details these calculations and Dr. Hugues Bodiguel has performed some numerical simulations to improve the numerical expansions.

We proceed with approximations and we rewrite the Equation 1.30. We envisage a steady state, with a meniscus velocity V . Away from the meniscus region, we assume the flow of the fluids to obey Poiseuille's law, and this allows to estimate the meniscus velocity as:

$$V = \frac{1}{\alpha} \frac{R^2}{\eta L} \left(p_\infty - \frac{2\gamma \cos \theta}{R} \right) \quad (1.32)$$

where p_∞ stands for $p(x \rightarrow -\infty)$ in the non wetting fluid. This equation ensures the momentum balance at the macroscopic interface. The pressure gradient in the non wetting phase is then simply given by $(p_\infty - 2\gamma \cos \theta / R) / L$.

Since the velocity is very small, we neglect the pressure gradient in the non-wetting phase. Standard lubrication approximation in the wetting film leads to (ref to Figure 1.10):

$$h_t + \frac{1}{\beta \eta} \frac{d}{dx} (h^3 p_x) = 0, \quad (1.33)$$

where β is a numerical factor with the exact value in Equation 1.30:

$$\beta = \frac{12(1-h)^2 + 12m \left(\frac{(3-h_\infty)(h+h_\infty) + (3m-2)h_\infty h}{2(1-h_\infty)^2 + 3mh_\infty(2-h_\infty)} - h^2 \right)}{(4(1-h)^2 + 3mh(1-h))} \quad (1.34)$$

Usual lubrication approximation is not valid at the meniscus. This should not be a problem here since the meniscus shape is circular except for small h , where $h_x \ll 1$.

It is then imperative to change the origin of the x -axis in order be in the frame of the meniscus. Writing $x' = x - V(t)t$, we get $h_t = V h_{x'}$. The previous equation transforms to:

$$V h_{x'} = -\frac{1}{\beta \eta} \frac{d}{dx'} (h^3 p_{x'}) \quad (1.35)$$

After one integration, it reduced to

$$V = -\frac{1}{\beta \eta} h^2 p_{x'} + \frac{C}{h} \quad (1.36)$$

C is, at this point, an unknown constant. It seems reasonable to assume that far from the meniscus, the film thickness will reaches a constant value h_∞ , and the pressure gradient should vanish, $p(x' = h_\infty) = 0$ leads to $C = V h_\infty$.

Using Equation 1.14 and switching to dimensionless quantities (distances normalized by R and pressures by γ/R), we obtain the following differential equation:

$$\beta Ca \left(1 - \frac{\tilde{h}_e}{\tilde{h}}\right) = \tilde{h}^2 \frac{d}{d\tilde{x}} \left[\frac{\tilde{h}_{\tilde{x}\tilde{x}}}{(1 + \tilde{h}_{\tilde{x}}^2)^{3/2}} + \tilde{\Pi}(\tilde{h}) \right] \quad (1.37)$$

with boundary conditions:

$$h(0) = 1 \quad (1.38)$$

$$h_x(0) = -\infty \quad (1.39)$$

$$h_x(\infty) = 0 \quad (1.40)$$

Once this equation is solved for a given Ca , the apparent contact angle $\cos \theta$ is given by the curvature at $x = 0$. Then Equation 1.32 could be used to determine the corresponding pressure p_∞ :

$$\tilde{p}_\infty = \frac{\alpha L}{R} Ca - \lim_{x \rightarrow 0} \frac{\tilde{h}_{\tilde{x}\tilde{x}}}{(1 + \tilde{h}_{\tilde{x}}^2)^{3/2}} \quad (1.41)$$

Note that the differential equation (Equation 1.37) is only valid for very low values of Ca (typically below 10^{-7}) and thus only aims at describing the hysteresis-like region between P_1 and P_2 .

1.4.2.4 Numerical results

In fact, the infinite thickness h_∞ does not need to be fixed at the equilibrium value but is an output of the calculation. Equation 1.37 is transformed using the substitution $y(h) = h_x$, and is solved for $h \in [h_\infty, 1]$, with boundary conditions $y(h_\infty) = 0$, $y'(h_\infty) = 0$ and $y(1) = -\infty$, where h_∞ is unknown. In practice, this equation is solved at fixed h_∞ with the first and second bound condition, and h_∞ is then varied to match the third one.

For the disjoining pressure, we use the Van der Waals forces with form displayed in Figure 1.10, with the following parameters : $A_{g/w} = -7 \times 10^{-9}$, $A_{g/o} = 1 \times 10^{-9}$, $d = 10^4$. These values correspond to standard values of Hamaker constants (in non dimensional units) and a plate separation of $100 \mu m$. The equilibrium contact angle is in this case $\cos \theta = 0.92$. Firstly, the meniscus profile $h(x)$ could be calculated for various capillary number Ca , sketched in Figure 1.18.

The meniscus goes with a wetting film for the $\beta Ca > 10^{-2.5}$, shown in Figure 1.19. Their thicknesses verify the Bretherton law, Equation 1.27. Compared with the Landau-Levich theory, Equation 1.26, we get the value of prefactor $\beta = 1.9$.

And for the small Ca ($\beta Ca < 10^{-2.5}$), the Cox-Voinov law, Equation 1.19, is valid as shown in Figure 1.20. Here, the logarithmic factor is about 1, which is quite low. It should be on the order of 7.

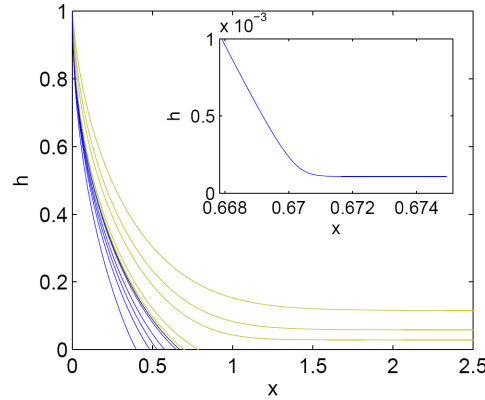


Figure 1.18: Profiles $h(x)$ for various Ca . Blue (left) curves correspond to negative values of Ca . In insert, magnified view of the equilibrium profile.

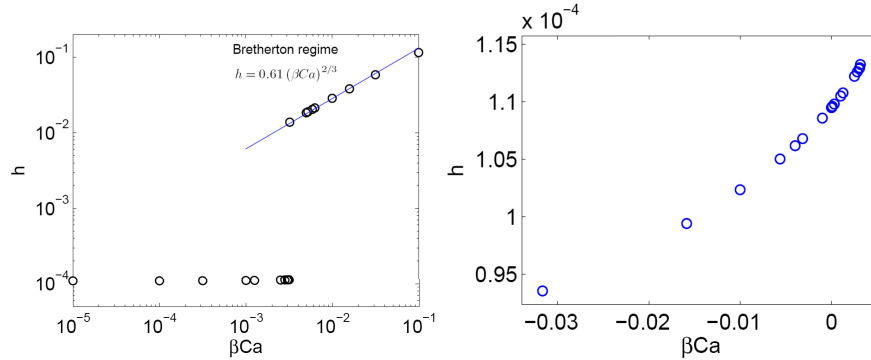


Figure 1.19: Film thickness as a function of Ca . Bretherton film are formed for $\beta Ca > 10^{-2.5}$ and the thicknesses are well accounted by the theoretical prediction. Identifying the prefactors leads to a value of $\beta = 1.9$.

It should be noted that when the parameters $A_{g/w}$, $A_{g/o}$, d and $\cos\theta$ vary, the results displayed in Figure 1.18, 1.19 and 1.20 do not change much. In summary, we recover Cox-Voinov law for low Ca , and Landau-Levitch films for high Ca , with a transition at $\theta = 0$. The disjoining pressure does not have any influence at the macroscopic scale, except concerning the equilibrium contact angle. No hysteresis-like plateau are reported. We will come back later on this point.

1.5 Conclusion

This overview of the literature demonstrates clearly that some important features of wetting dynamics are not yet understood. The dynamics of contact lines and contact angles in microscopic scales, specially between two immiscible liquids, is discussed in this thesis work. The wetting conditions, which contains partial, complete and pseudo-partial wetting, and

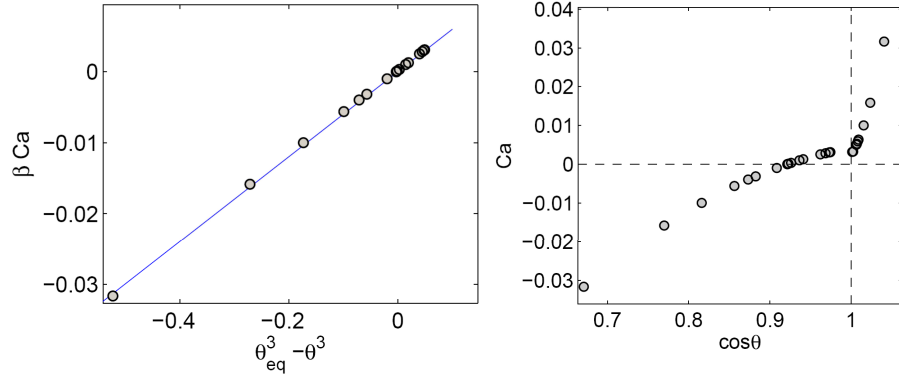


Figure 1.20: Ca as a function of the meniscus curvature $\cos\theta$.

the various geometries of channels are interested. In this work we plan to address the following questions.

Firsly, we adress to the concequences of the microscopic wetting films. Various experimental results show contact angle dynamics with velocities. And also indicate the systems activation energy to displace a interface. A general point of view among all the wetting systems is proposed. They distinguish each other from the different levels of activation energy.

Secondly, the wetting film in a corner under complete wetting situation is discussed. Its consequences are displayed in two situations: one has a crossed junction, the coupling of main pressure gradient and corner pressure gradient leads to the corner flow effects. The other one has a special design of microfluidic chip, the consequence of drainage is demonstrated and several quantitative relations are also modelled.

1.6 Summary

We define the wetting criteria on:

- The wetting behavior is a result of the molecular interactions between the liquids and the solid. It can be described using the spreading coefficient S and the Hamaker constant A . Three situations are encountered: complete, partial and pseudo-partial wettings.
- $S > 0$ and $A < 0$ lead to complete wetting. A wetting film of thickness h lies on the solid substrate. The three phases do not meet.
- Partial wetting corresponds to $S < 0$ and $A > 0$ or $A < 0$. The three phases meet on a line. We observe a macroscopic contact angle θ . Young's relation describes quantitatively the relation among the interfacial tensions γ and contact angle θ .
- Pseudo-partial wetting corresponds to $S > 0$ and $A > 0$. We observe a macroscopic contact angle θ that coexists with a microscopic wetting film h_∞ around the drop.

We study the shape of the interface in equilibrium and their properties.

- For a plate-plate geometry with distance h , the shape of contact line depends on wetting types.
- Under partial wetting situation, the static contact θ_e is comprised between the advancing angle θ_a and the receding angle θ_r . There is no wetting films and the three phases meet at the contact line. Displacement of the contact line occurs when θ is out of the interval $[\theta_r, \theta_a]$. The nature and the amplitude of the hysteresis zone is still poorly understood.
- Under complete and pseudo-partial wetting situation, the interface shape is complex because of the existence of microscopic wetting films, where we should consider the disjoining pressure $\Pi(h)$. Under complete wetting situation, the contact angle is $\theta = 180^\circ$ and h is set by $\Pi(h)$.
- In a complex geometry, wedges lead to the presence of wetting liquid in the corners.

Wetting dynamics

- The main parameters used to quantify the dynamics of wetting are relative velocity V and dynamic contact angle θ_d .
- In partial wetting situation, two models describe this dynamics: the hydrodynamic model and the molecular-kinetic theory. Some comparisons between models and experiments are presented for wetting dynamics. At this stage, there does not exist a comprehensive model describing all the cases reported in the literature.
- In pseudo-partial wetting, wetting film modifies the dynamics. Little is known concerning the dynamics properties of wetting and spreading in pseudo-partial wetting situation. The theory of forced displacement could describe the contact line profile under displacement by considering $\Pi(h)$. We note that taking into account $\Pi(h)$ does not predict an hysteresis-like plateau.
- In complete wetting situation, wetting films of a spreading droplet on a solid plate or in a capillary tube are discussed. Tanner's Law, LLD model and Bretherton's Law describe those situations, respectively.

Chapter 2

Materials and methods

This chapter addresses the different technology of microfabrications and several modifications of surface properties. At the end, methods of characterisation of liquid properties are also presented.

2.1 PDMS microfluidic chips

We report results obtained in PDMS (Polydimethylsiloxane) devices by using standard microfabrication techniques [78, 79]. This device is created in the elastomeric material poly(dimethylsiloxane) (PDMS), that makes it possible to carry out a complete cycle of design, fabrication (in less than 24 hours), and testing of microfluidic systems rapidly. It is chemically stable, but swells in the presence of certain oils. We have used a double photolithography method to fabricate a device with two layers of channels. We recall below the main steps of the procedure, which is sketched in Figure 2.1.

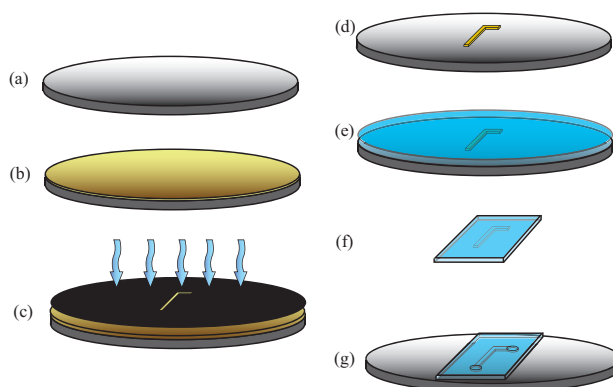


Figure 2.1: Illustration of fabrication of PDMS device. [80]

a) Wafer cleaning and spin coating. We use 3 inch silicon wafers, which are initially cleaned with acetone, then refluxed with isopropanol. Then, plasma cleaning (a cleaner

purchased from *Harrick*) is performed to remove organic residues and to active the substrate. A certain thickness h of negative photoresist resin is spin-coated on this wafer. There are two types of photosensitive polymers: positive and negative resins. Here, we use the negative resins SU-8 2050 (purchased from *MicroChem*): Ultraviolet radiation causes an exposed polymerization area and subsequently thermally cross-linked portions rendered insoluble to a liquid SU-8 developer, while the non-irradiated resin selectively disappears. With a spin coater, we use a rotation speed of 3000 rpm for 30 s with an acceleration of 300 rpm/s, and get a thickness about $h = 50 \mu m$.

b) Soft bake. The spin coated wafer is placed on a level hotplate with a good thermal control and uniformity (purchased from *SAVATEC*). The soft bake temperatures and duration vary with the thickness of film thicknesses. For $h = 50 \mu m$, the evaporation of solvent is during 3 minutes at $65^\circ C$ and then during 6 minutes at $95^\circ C$. And for $h = 150 \mu m$, the duration of soft bake is 5 minutes at $65^\circ C$ and then during 30 minutes at $95^\circ C$.

c) Ultraviolet exposure. A photomask, which gives the geometric features of the device, has the transparent channel areas and dark protected areas. The spin coated wafer is insulated through the photomask, which is placed above the wafer. The exposure energy depends on the film thickness, e.g., $200 mJ/cm^2$ for $h = 50 \mu m$, but $300 mJ/cm^2$ for $h = 150 \mu m$. To fabricate the multilayer channels, the step b) and c) are repeated with various rotation speeds and exposure time. It should be noted that the different patterns are superimposed precisely with mask aligner of *SUSS Micro Tec*.

d) Post exposure bake and development. The wafer is then baked directly after the exposure. After 1 minute, an image of the mask should be visible. The durations vary with the film thickness. For $h = 50 \mu m$, it takes 1 minute at $65^\circ C$ and 5 minutes at $95^\circ C$ and for $h = 150 \mu m$, it takes 1 minute at $65^\circ C$ and 10 minutes at $95^\circ C$. The development of exposed wafer takes place in immersion, spray or spray-puddle processes with SU-8 developer, which is usually PGMEA (polyethylene glycol monomethyl ether acetate), or ethyl lactate. The duration varies with the thickness, e.g., it takes 8 minutes for thickness of $200 \mu m$ and 4 minutes for $50 \mu m$. The wafer is sprayed and washed by isopropanol for approximately 10 seconds, followed by drying with nitrogen. After resin development, a positive resin relief on the wafer is obtained. A silanization of HMDS (hexamethyldisilazane) is performed as an adhesion promoter for resins.

e) Molding of PDMS. A 10:1 mixture of PDMS prepolymer and curing agent (Sylgard 184, *Dow Corning*) is stirred thoroughly and then degassed in a vacuum bell jar. The prepolymer mixture was poured onto the wafer from a petri dish and cured for 45 minutes at $65^\circ C$. The duration of curing and hardness depend on the ratio of prepolymer and curing agent.

f) Cutting of patterns. After curing, the PDMS replica was peeled from the mold of silicon. The inlets and outlets of microchannels are drilled with punches, whose diameter are chosen according the used injection tubes. We get a block of PDMS with a thickness of 5-6 mm, in which there's the micro channels with the shape on the photo mask. The piece of PDMS is cut around the pattern with channels.

g) Bonding of PDMS devices. To cover the micro channels, a glass slide is equally cleaned by organic solvent and plasma cleaner, and then spin coated with a thin layer of PDMS (at the order of dozen of micrometers), and cured for 45 minutes at 65 °C. The two pieces of PDMS were placed in a plasma cleaner and oxidized for 90 seconds. Immediately after removal from the plasma cleaner, the substrates were brought into conformal contact, and an irreversible seal formed spontaneously. Plasma modifies the surface properties of PDMS by the formation of carboxylic acids and a smooth, inorganic layer of silicon oxide. The formation of the carboxylic acids influences the wettability of the surface (to be hydrophilic) for about 12 hours and also provides scaffolding for further modifications [81]. To assure the bonding and wait the wetting property of surface to return hydrophobic, the sealed chip is left in the oven at 65 °C for more than 24 hours.

With these procedures, the microchannels have the four walls with the same materials, which leads to the same wetability. The bonding with plasma is resistant (during the manipulation, the local pressure arrive 2-3 bar) and sustainable (reusable).

2.2 Surface treatment: silanization

The surface property of glass capillary tube can be treated by chemical methods. Silanization is a method for organic thin film preparation and reduces the surface energy. It is used in a multitude of applications like coating for corrosion inhibition, adhesion promotion, anti-reflection, anti-statics, and biomolecule immobilization etc.

The principle of silanization is to cover the surface through self-assembly with organo-functional alkoxysilane molecules. It is a type of self-assembled monolayers (SAMs) [82]. The alkoxysilane contains at least one silicon-carbon bond, which is very stable and nonpolar. The presence of an alkyl group gives rise to low surface energy and hydrophobic effects, which means to vary the wetting properties. Mineral components like mica, glass and metal oxide surfaces can all be silanized, because they contain hydroxyl groups which attack and displace the alkoxy group on the silane thus forming a covalent $-Si-O-Si-$ bond [83]. Two types of grafting processes are used: vapor phase method and solvent method [84]. We have worked with the liquid method, the silane solution is injected in the glass capillary.

The surface coverage resulting from the silanization reactions depends on several variables such as nature of the solvent, temperature, reaction time, degree of hydration of the substrates, the cleaning procedure utilized prior to silanization of substrates, and the nature/morphology of the oxide layer on the substrate [85].

The solvent method is common because of its easier feasibility. Several solvents are used: toluene, carbon tetrachloride, hexadecane, fluorinated oil (*i.e.* FC-40), etc [84, 85].

Toluene is frequently used, because it is rather polar and can also be adsorbed on the silica surface and then prevents the silanol groups on the surface from reacting. As a consequence, it results in a lower grafting density. Carbon tetrachloride, which is less polar than toluene is less adsorbed on the silica surface, and as a consequence, higher contact angles and grafting densities can be observed [84]. Hexadecane favors the physisorption of silane on the solid substrate [86].

The temperature may play a role for it change the solvation and the adsorption of silane on the substrate. For example, the grafting of OTS (octadecyltrichlorosilane) in hexadecane solution, the optimum temperature is 18°C [86].

The surface concentration of silanes grows rapidly in the first few minutes in most of the studies [84, 87]. A duration too long favors the silanes condensation and polymerization, which cause the heterogeneities of the grafting [88]. Too high concentration of silane might also increase the condensation, that's why the solution is generally not concentrated (with the order of 10^{-2} or 10^{-3} mol/L).

In a clean, zero-aqueous environment, these silanes remain stable for long time periods (for years). But wherever there are even traces of water in the medium, the silanization processes immediately start to progress. Water initiates hydrolysis of initial compounds, which subsequently condensate (polymerize), shown in Figure 2.2 [88]. Therefore, it's imperative to silanize in an environment without water. The use of anhydrous solvent is one of variables to obtain a homogeneous grafting. Nevertheless, because of the humidity, silanization requires always a lot of delicate tests and precautions.

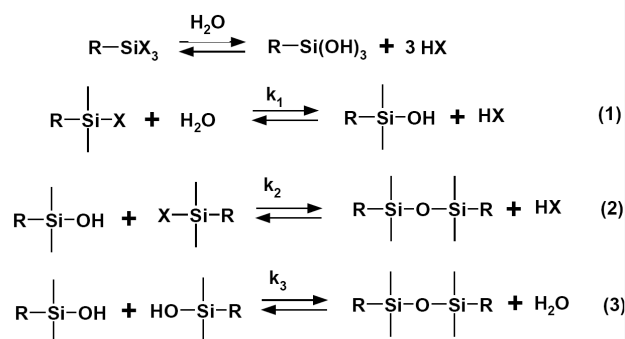


Figure 2.2: Hydrolysis and condensation of trifunctional silane [88].

2.2.1 Surface preparation

Two types of grafted glass surfaces have been considered in this thesis work: the lab microscopic slides and circular capillary tubes, which is a 10 cm glass circular tube of *VitroCom* with 0.20 mm inter diameter and 0.33 mm outer diameter. The cleaning procedure used prior to the silanization of the substrates is a crucial parameter involved in the variability of the grafting and structure of the layers. Before silanization, these were initially ultrasonically cleaned in acetone, then refluxed in isopropanol, and finally subjected to piranha

solution (1/2 hydrogen peroxide (33%), 1/2 sulphuric acid 97%) for 5-10 minutes. The Piranha solution is a highly oxidative, corrosive and possibly explosive chemical, which is used to remove organic residues from substrates. These glasses are rinsed with purified water (18 $M\Omega$, low organic content) and blown with dry nitrogen in a vacuum drying oven at 120°C. The rinsing and drying steps are important, because even the acid trace will degrade the silanes. Then, plasma cleaning is performed to remove organic residues and active the substrate.

Plasma cleaning involves the removal of impurities and contaminants from surfaces through the use of an energetic plasma created from gaseous species, such as argon and oxygen. The plasma is created by using high frequency voltages (typically kHz to >MHz) to ionise the low pressure gas (typically around 1/1000 atmospheric pressure). The substrate is then ready to graft the silanes.

2.2.2 Silanization: PFTS, OTS

Two types of silanes are used by solvent method: OTS (octadecyltrichlorosilane) and PFTS (1H,1H,2H,2H-Perfluorooctyl-trichlorosilane, called fluorinated silane).



Figure 2.3: Molecular structure of OTS and PFTS.

For the process of OTS silanization, we use the OTS in toluene with a concentration of 10⁻³% in mass. The solution is made to flow in the capillary tube or to immerse the glass slide during 30 minutes, rinsed with chloroform in an ultrasonic bath for 20 minutes, and then well rinsed by water. The capillary tube or slide is also put in a oven for hours to finalize the formation of covalent bond [85]. The substrate silanized by OTS is ready to use.

The silanization of PFTS is with a concentration of 5% by mass in fluorinated oil FC-40. This solution is made to flow in the capillary tube or to immerse the glass slide during 1 hour. The substrate is well rinsed with chloroform, ethanol and then water (with a duration of 20 minutes each time). The substrate silanized by PFTS is ready to use.

2.3 Resin SU-8 microfluidic chip

In many microfluidic applications identical channel wall properties are emphasized to ensure the uniform wetting or surface charging. As the PDMS chip deforms easily, and the oil could enter in the porous walls, we need a microfluidic chip to avoid these problems. Enclosed SU-8 microchannel devices [89, 90] are good choices. They are fabricated with the base of standard microfabrication techniques with resin SU-8. In Reference [91], SU-8 structures were sandwiched between silicon and glass wafers using SU-8 itself as an adhesive. Here,

we use the resin of SU-8 3000 series, which is an improved formulation of SU-8 2000, and has improved adhesion and reduced coating stress. Here, we recall some additional steps, compared with PDMS devices.

1) Mask This mask, sketched in the left part of Figure 2.4, is different from those for PDMS devices. Because the resin SU-8 for PDMS chip is used as a mold, but here the non-irradiated resin disappears and forms directly the channels. Special attentions have been paid to draw this mask. The filling of the channels by the adhesive SU-8 and breaking during the pressing period are the two main problems, that could occur during the process. A mask with an auxiliary structures (or moats) is designed, sketch in the left and middle parts of Figure 2.5. These moats could efficiently prevent the filling of the channels. The white transparent part allows the resin to be exposed, cross-linked and then to form the channels' walls. The contour of the white zone is much smaller than the wafer size, because during the step of soft bake, the initially isothick film will wrinkle its edge. A consequence is that the baked film has a thickness much important than the center. Such a thickness variation will easily break the wafer. In order to bond two pieces of wafers, we press them with a pressure of about 3.5×10^5 Pa.

The reduced white zone permit to take off the edge zone. The spiral zone is designed very compact to decrease the total surface of the channel zone. The reduced channel zone surface avoids efficiently the problem of breaking of the glass wafer during the bonding step. The red part is the channels, which has a spiral part and a linear branch. In the linear part there's a circle with two branches of different widths, which is zoomed in the middle part of Figure 2.5. The reason of asymmetric will be detailed later. Around the red channels, moats are designed in black in order to avoid the blocking of channels during the bonding step [89]. This design has been improved several times and efficiently prevent the totally or partially filling of unexposed SU-8.

2) Ordinary SU-8 process (a-d) Glass wafer cleaning, spin coating, soft bake, ultraviolet exposure and post exposure bake. We use a 3 inch glass wafer, which is ultrasonically cleaned in acetone, then refluxed in isopropanol, and finally subjected to piranha solution. This wafer is then well rinsed by purified water and dried with nitrogen. A rotation program with a speed of 3000 rpm for 30 s and an acceleration of 300 rpm/s is used to deposit a layer of 5 μm with resin SU-8 3005 and a layer of 50 μm with resin SU-8 3050. These two layers of resin SU-8 are spin-coated in series on the same wafer: the 50 μm layer is spin-coated after the steps of soft bake, ultraviolet exposure and post exposure of the 5 μm layer. The spin-coated wafer is soft baked at 95 °C during 2 mins for 5 μm and during 15 mins for 50 μm . The exposure energy for 5 μm is 100 mJ/cm^2 for the 1st layer without photomask. The layer 50 μm is exposed with 250 mJ/cm^2 with the detailed photomask. It takes 1 minute for the 5 μm layer and 5 minutes for the 50 μm layer at 95 °C for the post exposure bake.

3) Bonding layer preparation(e) Another glass wafer is prepared. The inlet and outlet are drilled with a sand blasting machine (purchased from *Arene blast*). The wafer is then well cleaned. Another layer of SU-8 (a 50% (by mass) mixture of SU-8 3005 and cyclopentanone) is spincoated with the same program as for the 5 μm layer. This wafer is partially soft baked during 40 s at 95 $^{\circ}\text{C}$.

4) Bonding(f) These two wafers are well aligned and bonded under pressure of 3.5 bar ($3.5 \times 10^5 \text{ Pa}$) on a hot plate with a ramp of increasing temperatures. 5 steps of temperatures from 45 $^{\circ}\text{C}$ to 105 $^{\circ}\text{C}$ with an increase of 15 $^{\circ}\text{C}$ is applied each 10 minutes. A plateau of 120 $^{\circ}\text{C}$ last for one hour, and then a ramp of decreasing temperatures from 120 $^{\circ}\text{C}$ to 45 $^{\circ}\text{C}$ with an decrease of 15 $^{\circ}\text{C}$ each 10 minutes. The glass transition temperature is around 200 $^{\circ}\text{C}$.

5) Bonding of connectors Once the two wafers are well bonded, the connectors NanoPort are bonded above the inlet and outlet by a epoxy adhesive *potecny* NOA61 (which is a photopolymer that will be cured when exposed to ultraviolet light).

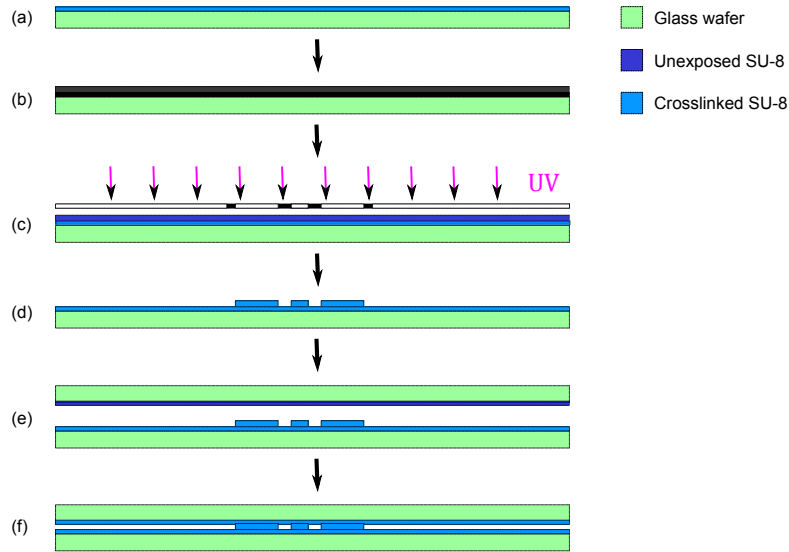


Figure 2.4: Main steps of microfabrications of SU-8 device. The steps (a) to (d) are the same with PDMS mold fabrication. The steps (e) and (f) are performed to bond two glass wafers to form the channels with all the walls in resin.

2.3.1 Wetting of SU8

The surface of the crosslinked SU-8 is hydrophobic and relatively flat (few roughness). The wetting properties with several liquids are tested. In order to characterize the wetting properties of SU-8, several couples of liquids are used to measure their contact angles θ .

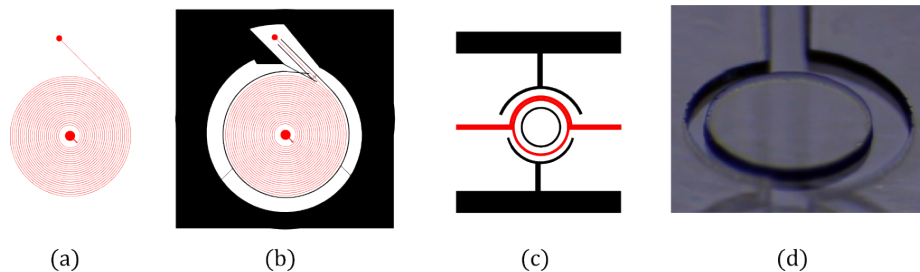


Figure 2.5: Mask and mold photo of the SU-8 device. (a) The expected chip motif for experiments of Chapter 7. (b) The real printed mask, with the channels (as the shape in (a)) and the moats around them. (c) Even around a circle with radius of $250 \mu m$, the moats are also needed. (d) the sharp wall of SU-8 mold.

As detailed in Figure 2.1, we measure the contact angles of droplets in the liquid/liquid/solid system. They are measured in a reservoir with two parallel transparent glass walls by a high resolution camera. Table 2.1 reports that the results obtained for various couples of fluids. As the rolling droplets could be the main reasons to determine a complete wetting system, we obtain complete wetting for several couples of liquids: FC-40/silicone oil V5, FC-40/dodecane, FC-72/silicone oil V20 and FC-70/dodecane. Their viscosity ratios are $M = 0.75, 2.5, 0.03, 17.9$, respectively. These complete wetting systems allow us to test the parameter M in the experiments of Chapter 7. Photos of rolling droplets are sketched in Figure 2.6.

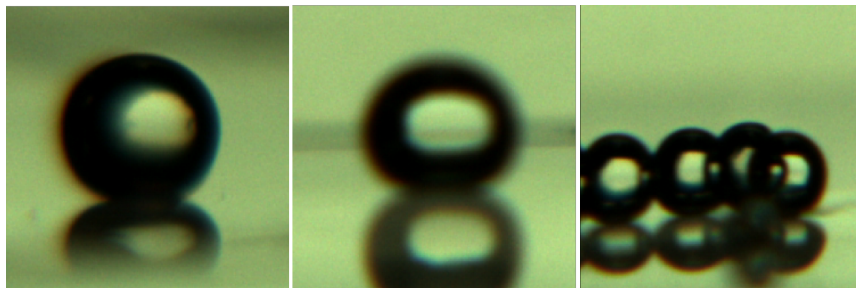


Figure 2.6: Photos of non-wetting droplet in a completely wetting liquid: FC-40/silicone oil V5, FC-40/dodecane and FC-72/dodecane.

2.4 Characterization of fluid properties

2.4.1 Viscosities of the used fluids

In this thesis work, several couples of fluids are used to form the interface. We have used dodecane, silicone oil V5, V20 (*Rhodorsil*) and paraffin oil as wetting liquids. The non-wetting ones are water, surfactant solution (TTAB, CTAB), aqueous glycerine solution,

phase 1	phase 2	contact angle(°)
dodecane	air	1.1
dodecane	water	14.0
silicone oil V5	air	0
silicone oil V20	air	0
silicone oil V20	water	60.4
silicone oil V20	dodecane	0
water	air	97.4
water	dodecane	119.6
water	silicone oil V5	123.3
TTAB solution	air	37.8
TTAB solution	dodecane	158.4
TTAB solution	silicone oil V5	166
FC-40	air	18.2
FC-40	water	83.6
FC-40	dodecane	180
FC-40	silicone oil V5	180
FC-40	silicone oil V20	
FC-72	dodecane	180
FC-72	silicone oil V5	139.4
FC-72	silicone oil V20	
FC-70	dodecane	180

Table 2.1: Contact angles of droplets of phase 1 in phase 2 on a plat SU-8 surface for various couples of liquids. TTAB solution stands for a concentration of 2.3×10^{-3} in mass. All the measurements are taken at around $T = 23^\circ C$. The contact angle displays the wetting properties. $\theta = 180^\circ$ means that the droplets roll easily, which indicates complete wetting systems.

fluorinated oil FC-40, FC-72 and FC-70. The properties are listed in Table 2.2. The viscosity of aqueous glycerine solution is detailed in Figure 2.7. We prepare this solution of a certain viscosity with this table and measure it with a rheometer (AR-G2, TA Instruments) with a cone plate geometry.

2.4.2 Interfacial tension measurement

Drop profile method The pendant drop method involves the determination of the drop profile of one liquid suspended in another liquid (or air) at mechanical equilibrium. This profile is determined by the balance between gravity and surface forces [93, 94].

$$\gamma(C - C_0) = \Delta\rho g z \quad (2.1)$$

Viscosity of Aqueous Glycerine Solutions in Centipoises/mPa s											
Glycerine per cent weight	Temperatur e (°C)										
	0	10	20	30	40	50	60	70	80	90	100
0 ⁽¹⁾	1.792	1.308	1.005	0.8007	0.6560	0.5494	0.4688	0.4061	0.3565	0.3165	0.2838
10	2.44	1.74	1.31	1.03	0.826	0.680	0.575	0.500	—	—	—
20	3.44	2.41	1.76	1.35	1.07	0.879	0.731	0.635	—	—	—
30	5.14	3.49	2.50	1.87	1.46	1.16	0.956	0.816	0.690	—	—
40	8.25	5.37	3.72	2.72	2.07	1.62	1.30	1.09	0.918	0.763	0.668
50	14.6	9.01	6.00	4.21	3.10	2.37	1.86	1.53	1.25	1.05	0.910
60	29.9	17.4	10.8	7.19	5.08	3.76	2.85	2.29	1.84	1.52	1.28
65	45.7	25.3	15.2	9.85	6.80	4.89	3.66	2.91	2.28	1.86	1.55
67	55.5	29.9	17.7	11.3	7.73	5.50	4.09	3.23	2.50	2.03	1.68
70	76	38.8	22.5	14.1	9.40	6.61	4.86	3.78	2.90	2.34	1.93
75	132	65.2	35.5	21.2	13.6	9.25	6.61	5.01	3.80	3.00	2.43
80	255	116	60.1	33.9	20.8	13.6	9.42	6.94	5.13	4.03	3.18
85	540	223	109	58	33.5	21.2	14.2	10.0	7.28	5.52	4.24
90	1310	498	219	109	60.0	35.5	22.5	15.5	11.0	7.93	6.00
91	1590	592	259	127	68.1	39.8	25.1	17.1	11.9	8.62	6.40
92	1950	729	310	147	78.3	44.8	28.0	19.0	13.1	9.46	6.82
93	2400	860	367	172	89	51.5	31.6	21.2	14.4	10.3	7.54
94	2930	1040	437	202	105	58.4	35.4	23.6	15.8	11.2	8.19
95	3690	1270	523	237	121	67.0	39.9	26.4	17.5	12.4	9.08
96	4600	1580	624	281	142	77.8	45.4	29.7	19.6	13.6	10.1
97	5770	1950	765	340	166	88.9	51.9	33.6	21.9	15.1	10.9
98	7370	2460	939	409	196	104	59.8	38.5	24.8	17.0	12.2
99	9420	3090	1150	500	235	122	69.1	43.6	27.8	19.0	13.3
100	12070	3900	1410	612	284	142	81.3	50.6	31.9	21.3	14.8

⁽¹⁾Viscosity of water taken from "Properties of Ordinary Water-Substance." N.E. Dorsey, p. 184. New York (1940)

Figure 2.7: Viscosity of aqueous glycerine solution [92], which is used to change the system's viscosity ratio M .

where C is the drop curvature at equilibrium, γ is the interfacial tension of liquid, C_0 is the curvature at $z = 0$, the apex of the droplet, $\Delta\rho$ is the density difference, and g is the gravitational acceleration. The drop is suspended axisymmetric around the axis z , the curvature C is expressed in cylindrical coordinates:

$$C = -\frac{r_{zz}}{(1 + r_z^2)^{3/2}} + \frac{r_z}{r(1 + r_z^2)^{1/2}} \quad (2.2)$$

with $r_z = dr/dz$ and $r_{zz} = d^2r/dz^2$.

The solution of Equation 2.1 gives the drop profile. The digitized profile of pendant drop at equilibrium is obtained by image analysis, and is then fitted by the solution of Equation 2.1, which allows to determine γ [95].

Practically, with the same reservoirs of measurement of contact angle, we measure the interfacial tension with droplet profile method between each couple of immiscible liquids.

Liquids	η	ρ	γ	$\theta(^{\circ})$ in air	
	($mPa \times s$)	($10^3 kg/m^3$)	(mN/m)	glass-OTS	PDMS
Water	1	1	72.8	106.2	92.2
Dodecane	1.34	0.75	25.35	7.3	18.6
Paraffin oil	26	0.84	28.50		58.5
Silicon oil V20	20	0.94	20.19		0
Silicon oil V5	5	0.91	10.73		0
FC-40	3.4	1.9	15.41	15	38.4
FC-72	0.6	1.68	12.76		
Glycerol TTAB	18	1.17	32.63		120
TTAB solution	1	1	37.77	60.3	
CTAB solution	1	1		120	

Table 2.2: Physical properties of used liquids at $T = 23^{\circ}C$. TTAB solution has a concentration of 2.7×10^{-3} and CTAB solution of 2×10^{-6} .

A home-made MATLAB program allows to fit the drop profile and the interfacial tension value. Table 2.3 represents all the used liquid-liquid interfacial tension in this thesis work.

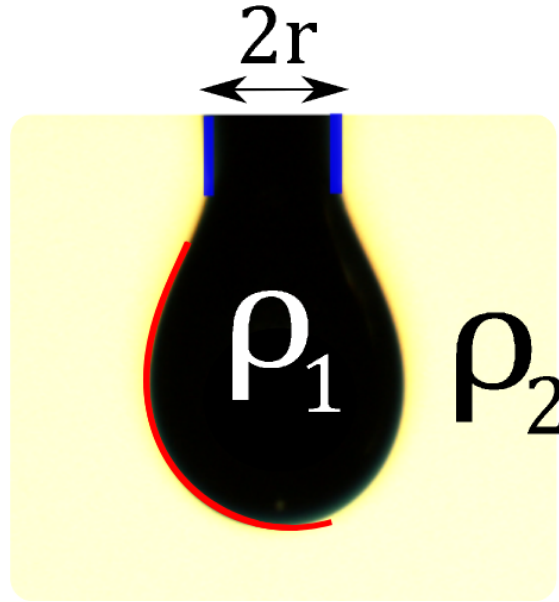


Figure 2.8: Measurement of interfacial tension with pendant drop method.

Drop weight method For very small interfacial tension, the profile method does not work. We need the drop weight method, which is another way to measure the interfacial tension. It relies on dripping a liquid of density ρ_i at a low flow rate from a capillary of out radius R into air or another liquid (with density ρ_e) and measuring the weight of drop that are formed. The method's origin can be traced to Tate [96], who postulated that the

drop's equilibrium among the drop weight ($F_W = mg$), the buoyant force $F_B = mg\rho_e/\rho_i$ and the surface force $F_\gamma = 2\pi R\gamma$, which is at the three phases contact line at the end of capillary. m is the drop mass, g is the gravitational acceleration and γ is the interfacial tension between the liquid and air or another liquid. The drop mass is usually measured by a mean value of dozen of drops. If the liquid in the capillary wets perfectly the capillary tube, drop's equilibrium at the moment when the drop is dripped is written:

$$mg\frac{\rho_e}{\rho_i} + 2\pi R\gamma = mg \quad (2.3)$$

Then the interfacial tension γ is under this form:

$$\gamma = \frac{mg\Delta\rho}{2\pi R\rho_i} \quad (2.4)$$

where $\Delta\rho = \rho_i - \rho_e$ is the density difference between two phases.

In reality, it is well known that only one portion of a pendant drop, which is grown from a dripping tip breaks away while a smaller fraction of the pendant drop remains undetached from the tip [97]. This inevitably results in smaller detached drop, or less weight, thus leading to an underestimation of the liquid interfacial tension. This problem is usually rectified by multiplying the calculated interfacial tension value with a factor that can be determined from an experimental curve developed by Harkins and Brown [98]. The curve is a plot of the fraction of the ideal drop volume, $f(R/V^{1/3}) = V/V_{Ideal}$, as a function of the dimensionless tip radius, $R/V^{1/3}$. Once the actual drop volume, V (and hence $R/V^{1/3}$), is known, the correction factor $f(R/V^{1/3})$ can be determined from the curve, and the interfacial tension can then calculated by

$$\gamma = \frac{mg\Delta\rho}{2\pi R\rho_i f(R/V^{1/3})} \quad (2.5)$$

Harkins and Brown's correction factor ranges with $R/V^{1/3}$ from 0.0638 to 4.45 and $f(R/V^{1/3})$ from 0.19 to 0.94. This method could achieve a precision of 0.1%.

$\gamma(mN/m)$	Dodecane	Silicone oil V20	Silicone oil V5
Water	48.2	33.81	41.87
TTAB solution	5.71	10.67	3.83
Glycerol TTAB	4.3372	3.19	2.47
FC-40	5.09	4.94	2.50
FC-72	2.14	4.42	1.60

Table 2.3: Concerned interfacial tension in this thesis work. TTAB solution has a concentration of 2.7×10^{-3} . Aqueous glycerol TTAB solution has a concentration of 2.25×10^{-3} and 70% of glycerol in mass. Two other interfacial tensions are also measured between dodecane with fluorescent dye (*KeyStone yellow 131SC*) and fluorinated oil FC-70 and FC-40: 4.32 and 3.13 mN/m .

2.5 Conclusion

We study the roles of wetting films and of corner flows in glass tubes and microfluidic chips. We use microfluidic chips and commercial glass tube, which are silanized to vary the wetting properties. For microfluidic chips, we have used two materials: resin SU-8 and PDMS. For all the devices, we were asked to test various couples of fluids that exhibit complete partial or pseudo-partial wettings. and study the microscopic wetting films under complete and pseudo-partial wetting conditions. The results are detailed in Chapter 3 and 4. The classical PDMS technics are used to fabricate the cross section channels in order to study the corner flows in Chapter 5. SU-8 chip is quite useful to study quantitatively the consequences of trapped clusters in Chapter 7.

2.6 Summary

PDMS microfluidic chips

- We presented the main steps involved in the microfabrication of PDMS chips.
- We use a cross junction to study the effect of corner flows and to impose drop of pressure on the invading but also on the prisoner fluid.

Glass surface treatments

- Silanization allows us to tune the energy of the surface and prepare hydrophobic surfaces.
- Two methods of silanization are used in this thesis work: PFTS, OTS.

Resin SU-8 microfluidic chip

- As oil enters the walls of the PDMS chip, we use a chip made of SU-8 resin.
- We present the main steps of microfabrication.
- We studied the wetting properties of SU-8 and found many fluids in complete wetting situations.

Characterization of liquid properties

- Viscosity and interfacial tension of studies systems are measured with various methods.

Part II

Meniscus dynamics in a circular tube

Chapter 3

Stationary states

3.1 Introduction

In this chapter we investigate various liquid-liquid meniscus dynamics. Their steady states of meniscus displacement are observed under different wetting systems: partial, complete and pseudo-partial wetting. The meniscus dynamics are studied in a glass circular capillary tube and controlled by pressure drops. We show that, contrary to air-liquid systems, pseudo-partial wetting is a quite common situation, provided that the solid surface is coated by a hydrophobic layer. This layer of coating leads results different from those for partial wetting and complete wetting. There is a hysteresis-like zone, which is a plateau zone but where the velocities are not zero. The width of the hysteresis zone varies for different systems. An interpretation of thermally activated depinning theory is proposed for the hysteresis zone in the discussion.

3.2 Experimental setup

The idea is to displace a liquid/liquid meniscus in a circular glass tube under an imposed pressure drop. The initial system is shown in Figure 3.1. It consists of a glass capillary tube, which is fixed on a glass support, two nanoports, which are used as an entrance and an exit of the two liquids, and two tubes, which are connected to two reservoirs. A pressure controller is connected to the tubes to control the liquid-liquid interface in the capillary tube. However the velocity measurements in this initial set up are not reproducible: A droplet of wetting liquid may become trapped in the entrance. This trapped liquid produces a dead volume, which affects the meniscus displacement under imposed pressure drops.

To prevent the formation of trapped droplets and the dead volume, an improved experimental setup is designed, sketched in Figure 3.2. It consists of two reservoirs connected by a horizontal circular glass tube with a radius of $R = 100 \mu\text{m}$ and a length of $L = 8 \text{ cm}$, which is commercialized by *VitroCom* (supplied by *CTS* from UK) and silanized by *OTS*(see 2.2.2). The tube is suspended in mid-air by drilling two small holes in each

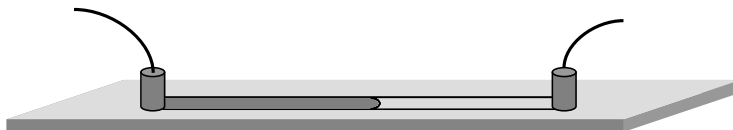


Figure 3.1: schematic drawing of the initial experimental setup.

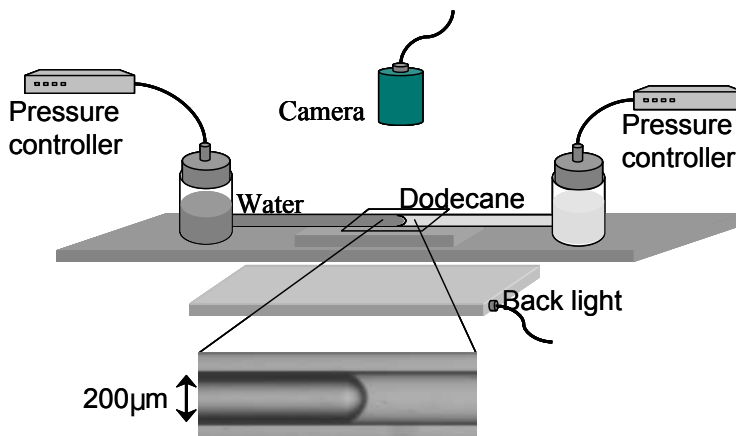


Figure 3.2: schematic drawing of the experimental setup.

reservoir. The two reservoirs are glass vials of 30 milliliter with the two holes about 1 cm high from the bottoms. These two reservoirs are filled with the immiscible liquids, one with a wetting liquid (dodecane), another with pure water. The capillary tube exceeds several millimeters in the interior of the two vials and are well bonded by epoxy adhesive at the holes. The two reservoirs are connected to a pressure controller which allows one to impose pressures precisely.

Starting from a situation where the wetting liquid is pushed by a pressure drop, the wetting liquid exceeds the tube and floats up in the vial, which is filled with water. The suspended capillary tube prevents the formation of dead volume efficiently. Once another pressure drop is applied to drive the meniscus into the tube, only one meniscus at a time is formed. The displacement of meniscus is recorded by a camera *AVT Pike F505B* mounted on a binocular *Olympus SZX16*. The meniscus velocity and its curvature are measured simultaneously, as a function of the applied pressure drop.

The displacement of the meniscus is extremely sensitive to small pressure drops variations. The liquid level change could also distort the measurement, as water of $h=1$ cm is equivalent to a pressure of 100 Pa. We should adjust the liquid levels to balance the liquid pressure. By taking account of their respective densities of oil and water, a ratio of height between water and dodecane is settled as $h_{\text{dodecane}}/h_{\text{water}}=1.33$. The big sectional area of vial is also chosen to avoid pressure distortion.

3.2.1 Pressure controlled flow

Pressure controlled flow plays an important role in microfluidics. The flow rate response time and stability are independent on the tubing and microsystems characteristics [99]. Pressure controlled flows allow one to precisely generate or manipulate the droplets [100–102], to manipulate particles and cells [103], to microfluidic applications in physics [104], in chemistry [105], in rheology [106,107].

Pressure controlled flow is chosen to study the meniscus dynamics in our experiments. Because we study the meniscus displacements and deformations with not only a stationary movement, but also the equilibrium states, which have zero velocities. With small velocities, the contact angle changes take place under equilibrium states with pressure control. In addition, to control the meniscus displacement with a quite low velocity in the order of $\mu\text{m/s}$, pressure control flow is more precise.

A commercially available pressure controller (*Fluigent MFCS 4C*) was used to drive independently the phases into the device, applying pressure patterns typically with accuracy of about 6 Pa in its measurement range from 0 to 2500 Pa. This multi channels output device provides a stable and pulseless flow with an instantaneous response time.

Why don't we choose the flow rate controlled flow? Current microfluidic manipulation systems such as syringe, peristaltic or piston pumps are poorly adapted to the manipulation of fluid volumes in the nanoliter range, leading to hysteresis, long equilibration times, irreproducibility and pulsing. For example, syringes pumps, which are widely used as flow rate controllers to push a liquid or gas, are driven via stepper motor and precision ball screw. Flow rate response time and stability strongly depend on tubing and microsystem characteristics. The accuracy of instantaneous flows in microchannels is poor due to hysteresis and connections compliance.

Furthermore, the flow rate control usually corresponds to a fixed non-zero velocity, which is not adapted to our experiments where the meniscus displacement is zero for a finite pressure drop (see later). Furthermore, because of mechanical limitation meant, we could hardly get small enough flow rate, e.g. several nanoliters per hour.

3.2.2 Different wetting systems

In order to vary the wetting properties, we use different couples of immiscible liquids on various solid substrates. The liquids couples consist of dodecane/aqueous solution and dodecane/fluorinated oil (FC-40). The liquids are flowed in glass tubes silanized either with octadecyltrichlorosilane (OTS) or 1H,1H,2H,2H-Perfluorooctyl-trichlorosilane (PFTS), and in Tygon tubes, purchased from VWR. All the chemical products were purchased from *Sigma-Aldrich*. We recall briefly the wetting studied here (detailed in Section 1.2).

Complete wetting is characterized by $S > 0$ and $A < 0$. At equilibrium, the droplet spreads out and form a film of uniform thickness covering the whole surface.

Partial wetting is characterized by $S < 0$. At equilibrium, the droplet does not spread and remains a lens (a macroscopic contact angle θ_e). There is usually contact line hysteresis in this wetting.

Pseudo-partial wetting has $S > 0$ and $A > 0$. However, compared with complete wetting, it exhibits an attractive interaction at long range between the solid ($A > 0$) and the non-wetting phase, and a repulsive interaction at short distances. In this situation, a macroscopic equilibrium contact angle θ_e coexists with a thin wetting film of thickness h_e .



Figure 3.3: Two equilibrium states of the glass-OTS/dodecane/water system. Left: A droplet of dodecane in water under a flat OTS-grafted glass plate exhibits a macroscopic contact angle $\theta_e = 40^\circ$. Right: a droplet of water in dodecane on the same surface does not stick to the surface $\theta_e = 180^\circ$. The droplets are about 1 mm diameter in both cases. Picture is taken by C. Cottin [80].

It is not straightforward to know a priori if a given system with spreading parameter $S > 0$, exhibits complete or pseudo-partial wetting. Indeed, it requires the knowledge of the disjoining pressure $\Pi(h)$ which contains various contributions, given the complexity of the used systems (aqueous solutions of surfactants, glass surface grafted with silane). It is however rather simple to experimentally distinguish pseudo-partial wetting from complete wetting. Under both wetting situations, if a drop of non-wetting phase is deposited on surface immersed in a wetting liquid, a spheric droplet stands on the surface and freely rolls on it when the surface is slightly tilted, as sketched in Figure 3.3.

However, if a drop of wetting phase is deposited on a surface immersed in the non-wetting liquid, the spreadings appear differently: for complete wetting, it reaches a very thin film slowly at long time. For pseudo-partial wetting, we observe a different behavior. Figure 3.3 shows two equilibrium states of glass-OTS/dodecane/water system of pseudo-partial wetting. The droplet spreads on the surface but reaches a steady state with a finite contact angle. Even after one week, the contact angle remains unchanged and it corresponds to an equilibrium state. Its spreading parameter $S_2 = \gamma_{gw} - (\gamma_{go} + \gamma_{wo})$ is negative in this situation. It exhibits an attractive interaction at long range between the solid (glass) and the non-wetting phase (water), and a repulsive interaction at short distances. In this situation, a macroscopic equilibrium contact angle θ_e coexists with a thin wetting film of thickness h_e . θ_e and h_e are related in equilibrium, but depend on the considered conditions. Such a configuration is only expected for pseudo-partial systems where the shape of the disjoining pressure in Figure 1.11 allows a coexistence between a thin wetting film and a macroscopic contact angle [14].

Table 3.1 summarizes the properties of the used systems. We determine for every couple of fluids the interfacial tension γ by the pendant drop method. The spreading parameter S is calculated with Young's equation Equation 1.7. Except for the glass-PFTS surface, all the systems exhibit a positive spreading parameter, meaning that there is always a wetting film of oil covering the surface. This is confirmed experimentally when trying to deposit a droplet of the non-wetting fluid on a planar solid surface immersed in the wetting fluid. Tygon/dodecane/FC-40 is distinguished as complete wetting, because its advancing and receding contact angle remain $\theta = 180^\circ$ and without hysteresis.

Systems	γ (N/m)	S (N/m)
Partial wetting		
glass-PFTS/dodecane/water	43.2×10^{-3}	-2.9×10^{-3}
Pseudo-partial wetting		
glass-OTS/dodecane/water	43.2×10^{-3}	2.4×10^{-3}
glass-OTS/dodecane/TTAB	5.8×10^{-3}	9.4×10^{-3}
glass-OTS/dodecane/FC-40	5.1×10^{-3}	11×10^{-3}
Tygon/dodecane/water	43.2×10^{-3}	> 0
Complete wetting		
Tygon/dodecane/FC-40	5.1×10^{-3}	> 0

Table 3.1: Measured interfacial tension and calculated spreading parameter S at 25° in the form "solid surface/wetting phase/non-wetting phase". TTAB stands for an aqueous solution of tetradecyltrimethylammonium bromide at 1.0×10^{-4} g/L (TTAB) or 4.1×10^{-3} (TTAB(II)). *Fluorinert* liquid FC-40 is a kind of electronic liquid, which is fully fluorinated with a molecular formula of $C_{21}F_{48}N_2$. The viscosities of the fluids are 0.89 mPa.s (all aqueous solutions), 3.4 mPa.s (FC-40) and 1.34 mPa.s (dodecane).

Limiting ourselves to the Van der Waals contribution to the surface interaction, we could anticipate the sign of the long range tail of disjoining pressure. It is given by the opposite of the sign of the Hamaker constant of the considered system by Brochard-Wyart *et al.* [14]. The solid surface consist of a very thin layer of silane covering a thick glass surface (see Section 2.2.2).

The particular shape of the disjoining pressure considered here, sketched in Figure 1.10, is obtained by a glass substrate grafted with a silane layer, wetted by dodecane in presence of water. This configuration produces the desired shape of the disjoining pressure, even when considering only Van der Waals interactions. Using combination relations for a stratified system that consist in a semi-infinite medium of glass (g), a layer of silane (s) of thickness d , a layer of dodecane (o) of thickness h and a semi-infinite medium of water (w), the long range potential $W(h) = \int_{\infty}^h \Pi \, dh$ of nonretarded Van der Waals interactions reads:

$$W(h) \simeq \frac{A_{w/g} - A_{w/s}}{(h + d)^2} + \frac{A_{w/s} - A_{w/o}}{h^2} \quad (3.1)$$

where A_{ij} are the Hamaker constant that can be deduced from the Hamaker constant of the pure components thanks to $A_{ij} = \sqrt{A_{ii}A_{jj}}$. In the considered case, the first term is

positive and prevails at short distance while the second is negative and prevails at long distance, leading to a minimum in W , and consequently to the shape of the disjoining pressure sketched in Figure 1.11.

For oil films much thicker than the silane layer thicknesses, the contribution from this layer could be neglected and the Hamaker constant of the system is approximated by $A_{g/o/w} = A_{g/w} - A_{w/o}$ (the indices g , o and w refers to the glass, oil and water phases, respectively). Using values from the literature [20], we find $A_{g/o/w} \simeq 4.5 \times 10^{-22}$ for glass/dodecane/water (we were not able to find the value for the systems involving Tygon tubes). This positive value is consistent with our observations, since for partial and pseudo-partial systems, the interaction is attractive at long distances, whereas it is repulsive for the systems exhibiting complete wetting.

3.3 Steady velocities

In this set of experiments, we focus on steady states of meniscus displacements in the experimental setup, which is described in Section 3.2. With the setup in Figure 3.2 under pressure control, the meniscus dynamics could be studied. In this simplest situation, the observed parameters of velocity, pressure and meniscus shape show the characteristics of the given system. For all the results reported here, we wait until a steady regime of velocities is reached. Special attention has been paid to perform the measurement a long time after the change of pressure, and to verify that the velocity is constant during the measurement.

In the following we will use non-dimensional quantities defined as $\tilde{P} = \Delta PR/2\gamma$ and $\tilde{V} = 4\bar{\eta}VL/\gamma R$, where $\bar{\eta} = (\eta_1 + \eta_2)/2$. $2\gamma/R$ is the capillary pressure and $\gamma R/4\bar{\eta}L$ is the characteristic velocity of a meniscus under a pressure drop equal to the capillary pressure.

3.3.1 Complete wetting

Figure 3.4 shows the results obtained with the systems in complete wetting. The complete wetting system of Tygon/dodecane/Fluorinert FC-40 exhibits a linear relation between $\tilde{V}$ and $\tilde{P}$, with a slope close to unity. Furthermore, $\tilde{V} = 0$ for $\tilde{P} \simeq 1$, showing that the macroscopic contact angle remains constant and equals 180° for receding and advancing menisci, which is confirmed by image analysis. The insert shows the graphic continuity of small velocities, which means there is no hysteresis zone. The meniscus image inserts indicate the uniform curvature for the advancing and receding menisci. The absence of velocities hysteresis and uniform curvature are two characteristics of the complete wetting system.

3.3.2 Partial wetting

The glass-PFTS/dodecane/water system leads to partial wetting. The meniscus velocity $\tilde{V}$ as a function of $\tilde{P}$ is sketched in Figure 3.5. There are two linear branches of slope in the

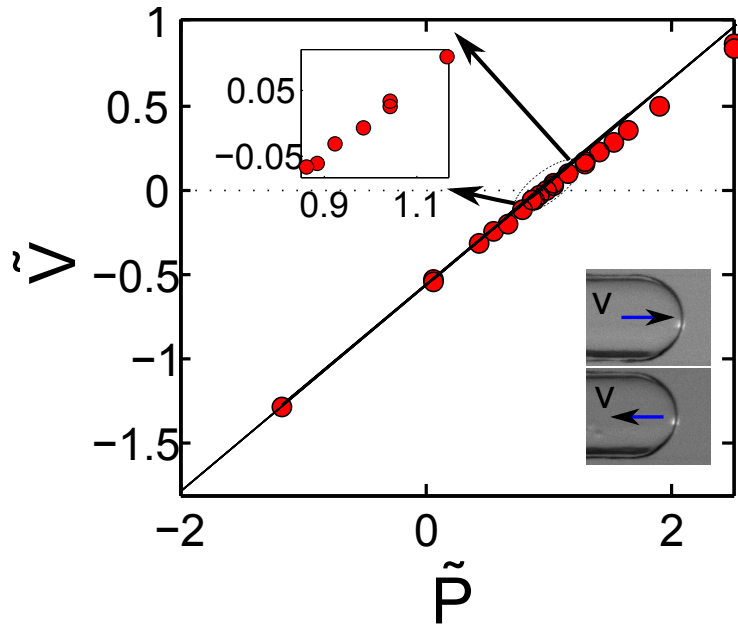


Figure 3.4: Non-dimensional meniscus velocity in steady state as a function of the pressure drop for the Tygon/dodecane/FC-40 system (complete wetting). The full lines represents $\tilde{V} = \tilde{P} - 1$. The meniscus image inserts show that the advancing and receding menisci keep the same curvature at small velocities.

order of unity, but separated by a pressure interval where the velocity vanishes. The contact line is pinned in this range of pressure. When the meniscus is moving, the contact angle coincide either to the advancing contact angle θ_a or to the receding one θ_r , which is verified by the measurement of the curvatures in the insert graphic between curvature C and $\tilde{P}$. Corresponding to the $\tilde{V} - \tilde{P}$ relation, the curvatures adjust themselves during the pinned zone ($\tilde{V}=0$). The contact angle varies in the pinned interval to accommodate the pressure difference that is imposed. The hysteresis is rather high (90°) for this system, probably due to an inhomogeneous grafting of the surface. We note that there are several non-zero velocities in the hysteresis zone, which may be a result of the inhomogeneous surface roughness at different positions of the tube. It should be remarked that the velocities in the edge of hysteresis zone are non zeros, which could be an effect of contact line hysteresis and will be detailed in the discussion.

3.3.3 Pseudo-partial wetting: glass-OTS/dodecane/water system

The meniscus velocity $\tilde{V}$ as a function of the pressure drop $\tilde{P}$ obtained with the glass-OTS/dodecane/water system is shown in Figure 3.6. The results look very similar to those of the partial wetting system discussed above: two linear branches are observed for $\tilde{P} < 0.6$ and $\tilde{P} > 1$, separated by a plateau where the velocity is very small (below $10 \mu\text{m/s}$). Contrary to what we observe for partial wetting, the velocity does not strictly

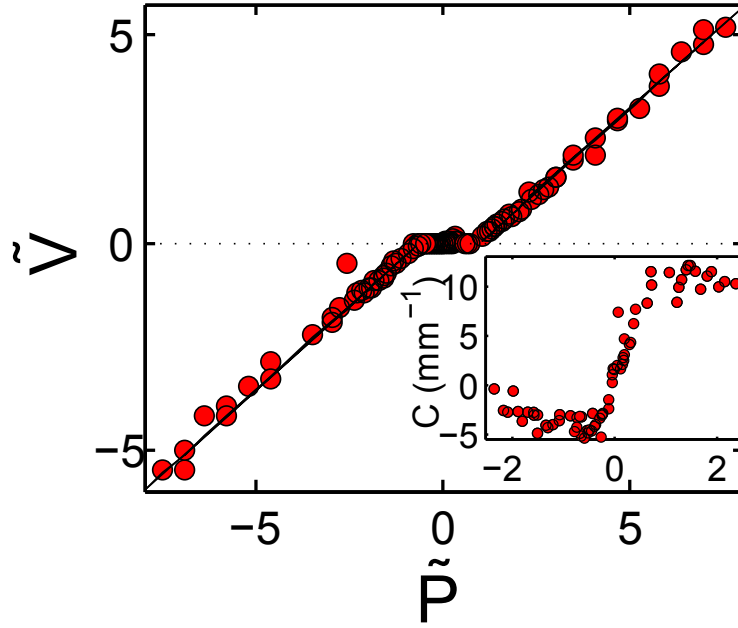


Figure 3.5: Non-dimensional meniscus velocity in steady state as a function of the pressure drop for the Glass-PFTS/dodecane/water system (partial wetting). There are two linear viscous regimes and a hysteresis plateau with $\tilde{V}=0$ or $\tilde{V} \approx 0$. The slope of each linear branch is 0.81.

vanish but is very small (see the insert in Figure 3.6), showing that there is no pinning. We call this plateau zone a hysteresis-like zone. Some experiments last even several days and we hardly ever find a meniscus pinned on the glass surface. Figure 3.7 shows one of the small and stable velocities, which keeps a $v=0.09 \mu\text{m/s}$ linearly during more than 16 hours under a $\tilde{P}=0.71$. We also observe that a pressure perturbation in this regime leads to a sudden move of the meniscus with a high velocity that eventually relaxes after some time, which is discussed in Chapter 4. Special attention has been paid to perform the measurement a long time after the change of pressure drop, and to verify that the velocity is constant during the measurement.

We observe the shape of the menisci in the plateau region. Figure 3.8 shows that the curvatures increase under reduced pressure drops $\tilde{P}$ from 0.52 to 1.04.

These observations show that although the stationary $\tilde{V} - \tilde{P}$ relation is at first sight similar to that of partial wetting, the mechanisms responsible for the plateau region are different. Let us recall that, for this system, $S > 0$, which means that there is always a wetting film of dodecane on the solid surface. The covered layer OTS modified the surface roughness, which may favor the existence for a wetting oil film. This film may be the reason of non-zero velocities. Further details are shown in the discussion.

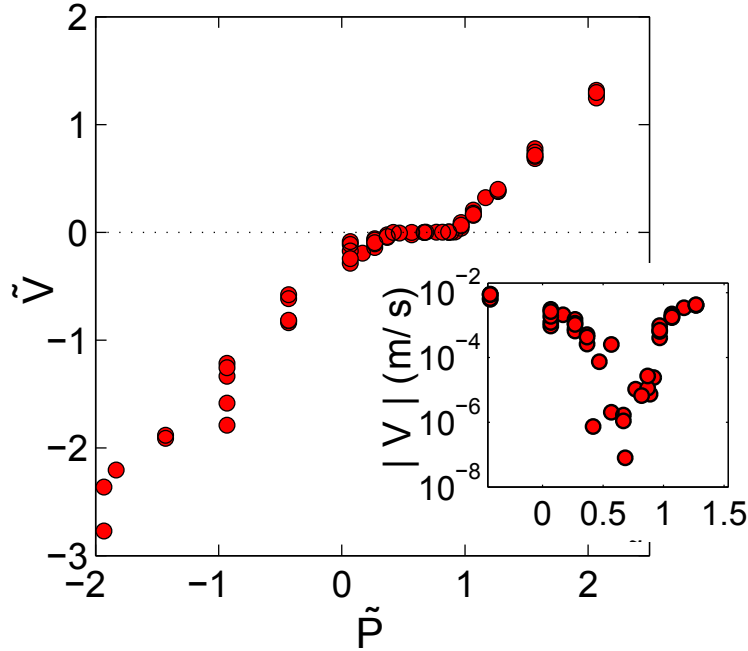


Figure 3.6: Meniscus velocity in steady state as function of the pressure drop for OTS/dodecane/water. The two linear branches have a slope of 1.1. Absolute values of non-vanishing velocities are shown in insert as a function of $\tilde{P}$, showing that the meniscus is not pinned but moves very slowly.

3.3.4 Other pseudo-partial wetting systems

The observations of pseudo-partial wetting system described above hold for all the other pseudo-partial wetting systems. Figure 3.9 displays the $\tilde{V} - \tilde{P}$ relation obtained for various aqueous solutions of standard surfactants against dodecane in OTS-grafted glass tube, together with the glass-OTS/dodecane/FC-40 and the Tygon/dodecane/water systems. All of these systems have a positive spreading parameter, and exhibit a hysteresis-like plateau where the velocity is very small but where the contact line is not pinned. The only difference between these systems is the pressure drop at which the meniscus starts to recede with a significant velocity (receding linear branch), which is indicated in the Figure 3.9. It thus seems natural to relate the observation of an contact angle hysteresis-like range without pinning to the pseudo-partial nature of the wetting for all of these systems. Our experimental setup is then a method to distinguish between pseudo-partial and complete wetting conditions.

3.4 Discussion

Using a simple set-up, we report velocity measurements of a single liquid-liquid meniscus in a tube in different wetting conditions under pressure control and at low capillary numbers.

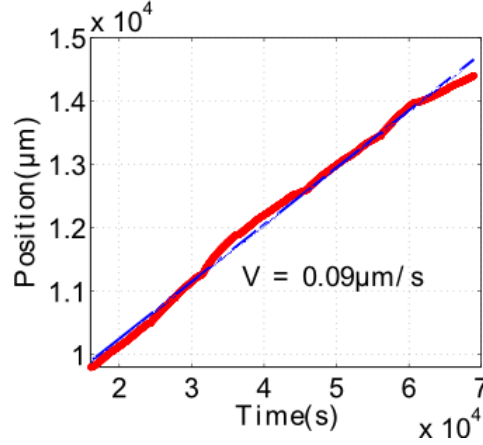


Figure 3.7: A stable displacement of a dodecane/water meniscus in a glass-OTS circular tube. It advances 4.5 mm during about 12 hours with a mean velocity $V = 0.09 \mu\text{m/s}$.

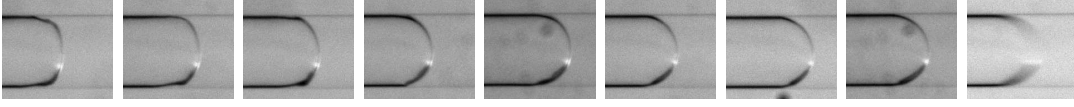


Figure 3.8: An illustration of curvature changes under pressure control for the glass-OTS/dodecane/water system. The images are taken for $\hat{P}=0.52, 0.58, 0.64, 0.69, 0.75, 0.86, 0.87, 0.96, 1.04$.

We observed three different behaviors. In the complete wetting situation, the velocity is proportional to the pressure drop and the contact angle remains constant and equal to 180° . In the pseudo-partial and partial situation, the velocity is proportional to the pressure drop for high absolute values of the velocity. In both case a plateau region in the vicinity of V equals zero separates the two hydrodynamic branches. In this region, the velocity is equal to zero in the partial wetting situation and is close to zero in the pseudo-partial wetting situation.

Our aim in the following is to understand how wetting theory captures these behaviors.

To compare our data with the model we need to measure the dynamic contact angle θ_d as a function of the velocity V . Indeed since the capillary tube is cylindrical, optical aberrations induce large error bars. To measure slight variations of the angle, we have chosen a hydrodynamic approach. We study the evolution of the meniscus velocity as a function of the pressure drop. In steady states, the pressure difference is the sum of the capillary pressure and the viscous pressure drop corresponding to Poiseuille flow, in the region that is far from the meniscus. Due to the high aspect ratio of the tube, both end effects and the meniscus region can be neglected so that the pressure difference is given by

$$\Delta P = -2 \frac{\gamma \cos \theta_d}{R} + \frac{8VL}{R^2} [\eta_1 x + \eta_2 (1 - x)] \quad (3.2)$$

where L is the tube length, V is the meniscus velocity, which also corresponds to the mean

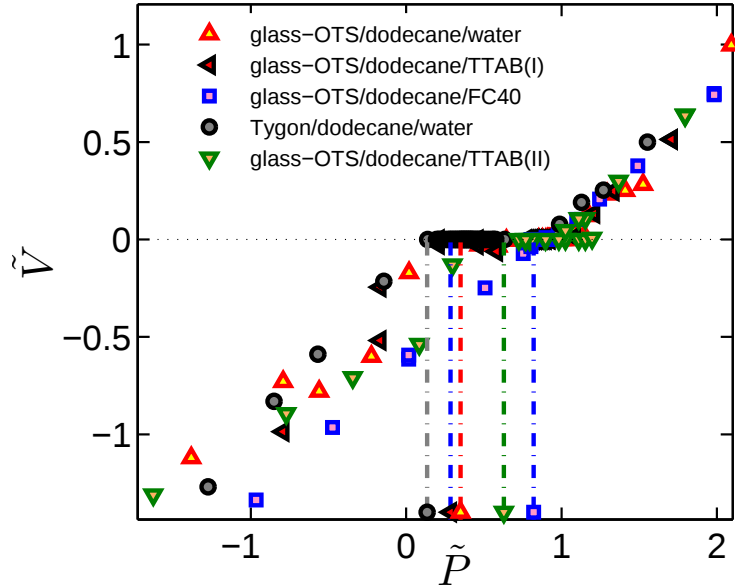


Figure 3.9: $\tilde{V} - \tilde{P}$ relations for various pseudo-partial wetting systems that have a positive spreading parameter (see table 3.1). The pressure corresponding to the end of the receding linear branch is highlighted by vertical dashed lines. The concentrations for the solutions of surfactants are 1×10^{-4} for TTAB(I) and 4.1×10^{-3} .

velocity in the tube, η_1 and η_2 are the viscosities of the two fluids, and x is the reduced position of the meniscus inside the tube, which is normalized by L . The contact angle θ_d is defined in the non-wetting phase. Using thereafter non-dimensional quantities defined by $\tilde{P} = \Delta PR/2\gamma$ and $\tilde{V} = 4\bar{\eta}VL/\gamma R$, where $\bar{\eta} = (\eta_1 + \eta_2)/2$ the previous equation reduces to

$$\tilde{P} = -\cos \theta_d + \tilde{V} \frac{[\eta_1 x + \eta_2 (1 - x)]}{\bar{\eta}} = -\cos \theta_d + a\tilde{V} \quad (3.3)$$

Since x is set around 0.5 and do not vary significantly during the experiments, a is close to one. However its exact value is at this stage unknown.

To extract a and θ_d we use the following procedure. In our experiments, θ_d may vary in the vicinity of zero velocity but remains constant for high velocities. Indeed, we investigate regions characterized by very small capillary numbers (typically between 10^{-9} and 10^{-4}). Hydrodynamic forces do not induce a variation of the contact angle. Assuming that θ_d does not depend upon $\tilde{V}$ for large $\tilde{V}$ in our experiments, we measure a . a is simply the slope of the curve $\tilde{P}$ as a function of $\tilde{V}$. We recall that for high velocities, all the experimental data display a linear evolution of the velocity as a function of the pressure.

Knowing a , we then deduce:

$$\cos \theta_d = a\tilde{V} - \tilde{P} \quad (3.4)$$

3.4.1 Comparison with the wetting dynamics theory: the hydrodynamic approach

We first check that hydrodynamics plays no role in the evolution of the contact angle. We calculated the value of the fitting parameter $\ln(L/l_m)$ for the FC-40 system using Equation 1.19.

We found that $\ln(L/l_m)$ is larger than 10^5 , as sketched in Fig 3.10. In the Cox model L is the distance from the solid at which the solution is truncated. l_m is the slip length. In the literature, L is typically around $10 \mu m$ and l_m around $1 nm$. This leads to a value of the fitting parameter around 10 [52]. $\ln(L/l_m)$ in our study we find very large values of $\ln(L/l_m)$ that do not make sense.

Thus for the low Ca investigated here, this hydrodynamic approach does not describe our experimental results.

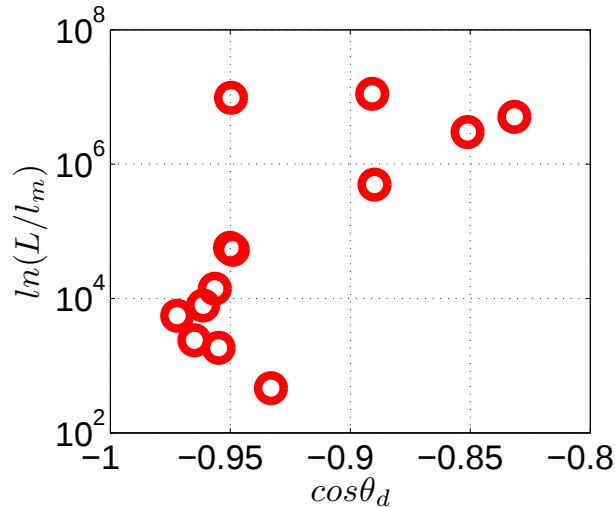


Figure 3.10: $\ln(L/l_m)$ as a function of θ_d for the pseudo-partial wetting system FC-40

3.4.2 Comparison with the wetting dynamics theory: the thermally activated depinning theory

In the following, we will compare these data with thermally activated depinning theory. Assuming that the advancing and receding phase are not symmetric the model predicts:

$$\tilde{V} = \begin{cases} A_a \sinh(B_a(\cos\theta_e - \tilde{P} + \tilde{V})), & \tilde{V} > 0 \\ A_r \sinh(B_r(\cos\theta_e - \tilde{P} + \tilde{V})), & \tilde{V} < 0 \end{cases} \quad (3.5)$$

with

$$\begin{aligned} A_{a,r} &= \lambda_{a,r} \nu_0 e^{-\frac{E_{a,r}^*}{k_B T}} \\ B_{a,r} &= \frac{\lambda_{a,r}^2 \gamma}{2k_B T} \end{aligned}$$

A mean activation energy ϵ^* can be defined as

$$\epsilon^* = E_a^*/\lambda_a^2 + E_r^*/\lambda_r^2 \quad (3.6)$$

The interesting point in this model is that a single physical mechanism controls both the hysteresis (or the pinning) of the contact line and its dynamics at the depinning threshold: the activated regime is nothing but a thermal rounding of the depinning transition, as sketched in Figure 1.14. Hence, one expects that the hysteresis $H = \gamma(\cos\theta_r - \cos\theta_a)$, where θ_a is the advancing angle and θ_r is the receding one, scales like ϵ^* .

The effectiveness of a given model is usually assessed by fitting the experimental data to the relevant equation with its free parameters, as given in Table 1, where θ_e is the only measurable parameter. To evaluate its effectiveness, the first criteria is to calculate the error between the experimental data and the best fit.

In our situation, we will not follow this standard procedure. Our experimental data are noisy. Due to some inaccurate measurements of the velocity or of the hydrodynamic resistance, Equation 3.4 may lead to values for the cosines of the contact angle higher than 1 or smaller than -1. Such points force us to abandon a classical procedure.

In the following, we will set θ_e to the middle of the hysteresis plateau. Under those conditions, we are left with two fitting parameters. For a given λ we will set the value of the energy E^* that allow us to describe the range of the hysteresis plateau. Then we will select the parameter couple (λ, E^*) that fit the low velocities values. The choice will be made manually by comparing the figures displaying the experimental data and the model. Figure 3.12 and 3.13 will demonstrate that we may trust the fitted values of the parameters even this procedure is not straightforward.

3.4.3 Complete wetting

We consider firstly the complete wetting situation. Our data does not show a hysteresis zone. Figure 3.11 displays the evolution of $\tilde{V}$ as a function of $\cos\theta_d$. The data are noisy. They show that the contact angle remains constant. One may wonder if such data can be fitted with the molecular-kinetic model. Coming back to the origin of the model, we may write that for low values of the force f , V is proportional to f . f is given by the difference between the two contact angles. It may also be written as the difference between the pressure drop in the meniscus region and the capillary pressure.

We thus get :

$$\tilde{V} = 4\bar{\eta}A_aB_afL/\gamma^2R^2 = (A_aB_a4\bar{\eta}/\gamma^2R^2)(\tilde{P}_m - 1) = K(\tilde{P}_m - 1) \quad (3.7)$$

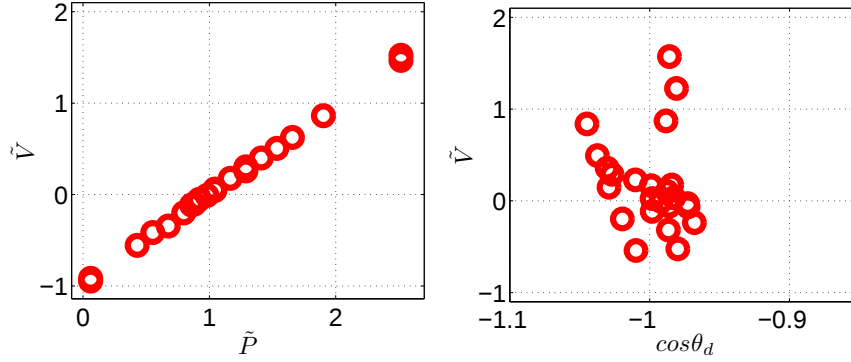


Figure 3.11: $\tilde{V}$ as a function of $\cos\theta_d$ for a complete wetting system. The values of $\cos\theta_d$ around -1 means the constant θ_d .

Where $\tilde{P}_m$ is the pressure drop in the meniscus zone. Let us note $\tilde{P}_c$ the dimensionless pressure drop due to viscous dissipation in the two liquids .

As $\tilde{P} = \tilde{P}_m + \tilde{P}_c$ and $\tilde{P}_c = a\tilde{V}$ we get

$$\tilde{P} = \tilde{V}((1/K) + a) + 1 \quad (3.8)$$

a has been defined before.

This set of equation shows that the molecular-kinetic model predicts a linear behavior in this case. However, due to the lack of precision on the determination of the hydrodynamic resistance, we are not able to extract the value of K .

3.4.4 Partial wetting

We consider partial wetting. Figure 3.12 displays the evolution of $\tilde{V}$ as a function of $\cos\theta_d$. The data display a zone where the velocity is equal zero.

The data are well described by the molecular-kinetic model. In order to capture the zero velocities, λ larger than 5 nm are required. This induces that the energy is larger than 120 $k_B T$. This energy is very large.

3.4.5 Pseudo-partial wetting

Pseudo-partial wetting has a non-zero velocity plateau, which is different from partial wetting. These non-zero velocities could be described and fitted by the Rolley model. We have worked with pseudo-partial wetting systems: *FC-40*, *Water*, *TTAB*, *TTAB(II)*, *CTAB*, *Water-Tygon*. Figure 3.13 display the experimental data and the fit. The data are reported using linear or logarithmic coordinates. This allows us to check the quality of the fit and to choose the parameters that describe the hysteresis boundaries but also report the values of the velocities in the plateau region.

We note that the obtained values for E^* are smaller in the pseudo-partial situation than in the partial one. The values of λ are around a few nanometers as previously. The

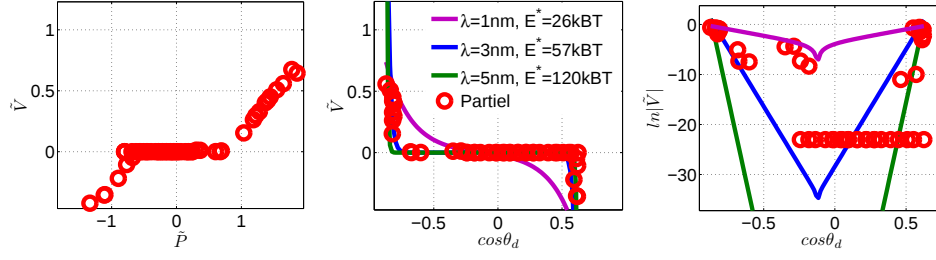


Figure 3.12: $\tilde{V}$ as a function of $\cos\theta_d$ for a partial wetting system. The red circles are experimental. The three solid lines are traced with theoretical values for three couples of parameters of λ and E^* . In order to capture the zero velocities, we decide to choose values of λ larger than 5 nm and E^* equals $120 \text{ k}_B T$. The zero velocities are set as $\tilde{V} = 10^{-23}$.

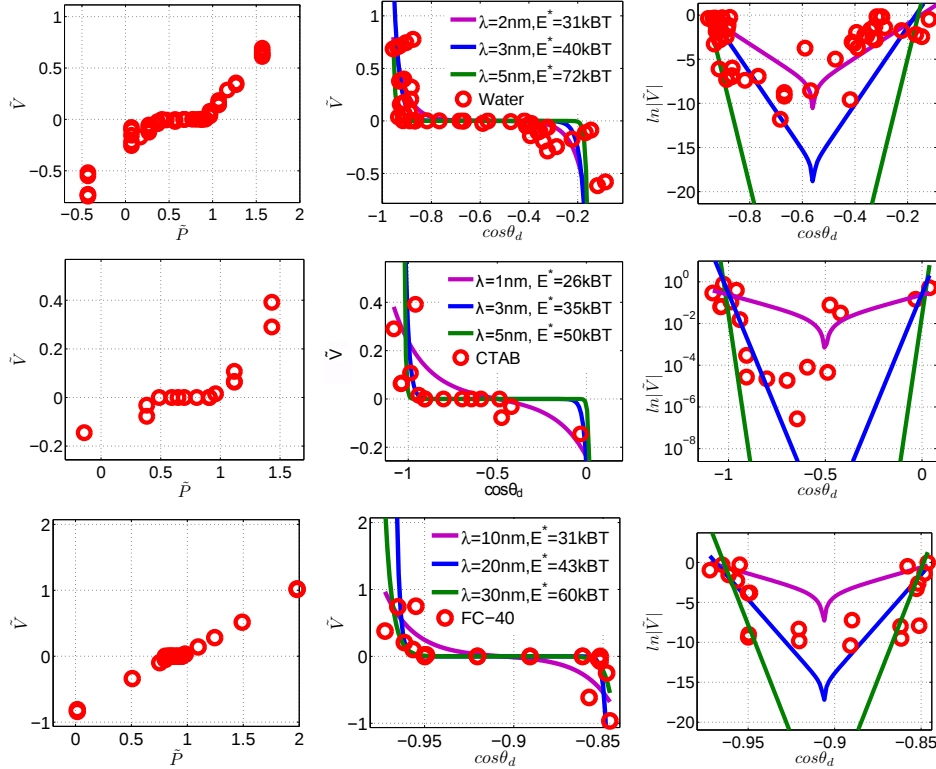


Figure 3.13: Three pseudo-partial wetting system *Water*, *CTAB* and *FC-40*. The solid lines are theoretical with three couples of parameter λ and E^* .

FC-40 system exhibits very large values of λ . This suggests that the surface displays less defects.

Following the approach of Rolley [19], Figure 3.14 displays the evolution of the normalized energy ϵ^*/γ as a function of the normalized hysteresis parameter $\cos\theta_r - \cos\theta_a$. We note that these parameters are proportional. Moreover they collapse on a line close to the

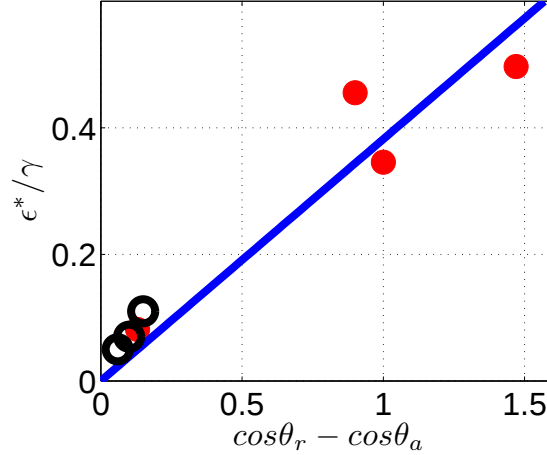


Figure 3.14: Normalized mean activation energy ϵ^*/γ as a function of the normalized hysteresis H/γ , red symbols are our experiments and black symbols from Rolley [19].

Systems	θ_e ($^\circ$)	λ (nm)	$E^*/(k_B T)$
Partial	97	5	120
Water	124	3	40
CTAB	150	3	35
FC-40	165	20	43

Table 3.2: Tested parameters for the partial and pseudo-partial wetting systems. θ_e , λ and E^* are the fitted parameters.

one previously measured by Rolley on other surfaces with other fluids.

This suggests that the pinning of the contact line on mesoscopic defects is likely to control both the wetting hysteresis and the activated dynamics which is observed close to the depinning threshold.

3.5 Conclusion

In this simple set-up, by changing the surface property and liquid couples, the property of the three-phase system and of the surface are discussed. We study the dynamics of liquid-liquid menisci in a circular tube at small capillary numbers in partial, pseudo-partial and complete wetting conditions. In the treated glass tube inner surface, there exists a thin wetting film in the last two situations. We precisely control the displacement of two immiscible liquids to observe the meniscus velocities, contact angles as a function of pressure drop. In pseudo-partial wetting condition, we observe that there is a pressure range where the velocity is extremely low (below $10 \mu m/s$) but non zero, in contrast with partial wetting, where the meniscus is blocked by a pinned contact line corresponding to the standard contact angle hysteresis. The role of surface heterogeneity is discussed to

explain the observations.

From these data, we have extracted the link between the contact angle θ_d and the velocity $\tilde{V}$. We show that the molecular-kinetic model describes the evolution of the contact angle θ_d in all the situations : complete, pseudo-partial and partial wetting. λ is roughly constant and equal to a few nanometers. The energy value depends upon the wetting situation. It is large in the partial wetting situation ($120 k_B T$) and around $40 k_B T$ for the pseudo-partial wetting situation.

3.6 Summary

Experimental setup

- An inner surface treated capillary tube is suspended in mid-air between two reservoirs. Two pressures are applied to an unique interface. The meniscus velocity V and its curvature are measured as a function of the applied pressure drop P .
- One of the advantages of this setup is to avoid the dead volume and droplets. The pressure controller has an accuracy of about $6 Pa$, which allow us to study displacement with low velocity.
- Glass surface treatment silanization allows us to obtain various wetting types: partial, complete and pseudo-partial wettings.

Stationary movement of liquid-liquid meniscus

- In complete wetting situation, V is proportional to the drop of pressure and vanishes at the capillary pressure.
- In partial wetting situation, V equals zero in the hysteresis-like plateau . In the high-pressure regime, the velocity and the drop of pressure are proportional.
- In pseudo-partial wetting situation, we observed a hysteresis-like plateau, which has non-zero velocities. The curvature variations in the hysteresis-like plateau are also displayed.

Comparison with thermally activated depinning theory

- Dynamics of contact angle can't be described by hydrodynamic approach.
- The thermally activated depinning theory captures dynamics in the complete wetting, partial and pseudo partial wetting situations.
- For the various pseudo-partial and partial wetting system, the parameters of disorder length λ and activation energy E^* could be measured by fitting the relation between $\tilde{V}$ and $\cos\theta_d$. The activation energy of partial system is larger than the one of the pseudo partial system. λ increases when the hysteresis decreases suggesting that surfaces displaying less hysteresis have less defects.

Dynamics of liquid-liquid menisci in pseudo-partial wetting

Lingguo Du, Hugues Bodiguel, Christophe Cottin, Annie Colin

Université de Bordeaux, Université Bordeaux 1, IPB, Rhodia, LOF CNRS UMR528
178 Avenue du Docteur Schweitzer, 33608 Pessac Cedex, France

Abstract

We study the dynamics of liquid-liquid menisci in a circular tube at small capillary numbers in partial, pseudo-partial and complete wetting conditions. There exists a thin wetting film in the last two situations. By pseudo-partial wetting, we refer to systems having non-monotonic disjoining pressures, as described by Brochard-Wyart *et al.*, Langmuir 7, 335-338 (1991). In this situation, the disjoining pressure allows the coexistence of a microscopic thin film (but not molecular) and a macroscopic contact angle. We measure the meniscus velocity as a function of the pressure drop for different wetting conditions. In pseudo-partial wetting condition, we observe that there is a pressure range where the velocity is extremely low (below $1\mu\text{m/s}$) but non zero, in contrast with partial wetting, where the meniscus is blocked by a pinned contact line corresponding to the standard contact angle hysteresis. The role of quasi-equilibrium and of surface heterogeneity is discussed to explain the observations.

Keywords: Liquid-liquid meniscus, Wetting film, Pseudo-partial wetting, Contact angle hysteresis

1. Introduction

When a droplet spreads on an ideal solid surface, two different types of wetting appear, designed as partial and complete wetting. These can be described by the spreading parameter, $S = \gamma_{SG} - (\gamma_{SL} + \gamma_{LG})$, which is the difference between the energy of a dried solid and that of a solid covered by a macroscopic layer of liquid [1] (γ_{SG} , γ_{SL} and γ_{LG} are the solid-gas, solid-liquid and liquid-gas surface tensions, respectively). There is partial wetting for $S < 0$, the liquid forms a drop with a finite contact angle θ , and complete wetting for $S > 0$, the liquid spreads completely to minimize its energy.

When the thickness of the liquid film is very small, one needs to consider the contribution of long range interactions in the energy balance. This is accounted in the literature by the introduction of Derjaguin's disjoining pressure Π [2]. Depending on the particular shape of $\Pi(h)$, Brochard-Wyart *et al.* [3] predicted another type of wetting designed as pseudo-partial wetting, for which the interaction between solid and non-wetting phase (usually air) is attractive at long range and repulsive at short distances. In this situation, a macroscopic equilibrium contact angle θ_e coexists with a thin wetting film of thickness h_e . These two quantities are related at equilibrium, but depend on the conditions considered (fixed volume, fixed pressure, size of the droplet...) [4].

From an experimental point of view, pseudo-partial wetting has been observed with a rather limited number of systems[5, 6, 7, 8, 9, 10]: brine-AOT/alkane/air, water/PDMS/air and water/alkane/air. Despite these few examples, this type of wetting has inspired several theoretical work that focused on the shape of interface from the macroscopic scale to the microscopic one [4, 11, 12]. Little is known however concerning the dynamics properties of wetting and spreading in this wetting situa-

tion. Since it is an intermediate situation between partial wetting where contact angle hysteresis plays an important role at low velocities, and complete wetting where there is no hysteresis, the description of the dynamics in pseudo-partial wetting asks for experimental studies.

In this work we investigate various liquid-liquid systems and show that, contrary to air-liquid systems, pseudo-partial wetting is a quite common situation, provided that the solid surface is coated by an hydrophobic layer. We focus on the steady state of meniscus velocity in circular tubes under pressure control and discuss the difference between the three types of wetting situations: partial, complete and pseudo-partial wetting.

2. Material and methods

2.1. Systems

In order to vary the wetting properties, we use different couples of immiscible liquids that consist in dodecane and an aqueous solution or a fluorinated oil (FC-40). They are used in glass tubes silanized either with octadecyltrichlorosilane (OTS) or 1H,1H,2H,2H-Perfluorooctyl-trichlorosilane (PFTS), and in Tygon tubes, purchased from VWR. All the chemical products were purchased from Sigma-Aldrich. Table 1 summarizes the properties of the systems used. We determine for every couples of fluids the surface tension γ using the pendant drop method. The spreading coefficient S is defined by $S = \gamma_{sw} - \gamma_{so} - \gamma$, where γ_{so} and γ_{sw} are the surface tensions of the oil / solid interface and of the aqueous solution / solid interface, respectively. It is determined by using contact angle measurements of a drop of oil on the solid surface in air, and a drop of water in the same conditions. A simple combination of Young's law then allow to deduce the value of S . The sign of S is used to distinguish partial wetting systems ($S < 0$) from complete or pseudo-partial

wetting ($S > 0$). Except for the glass-PFTS surface, all the systems exhibit a positive spreading coefficient, meaning that there is always a film of oil covering the surface. This is confirmed experimentally when trying to deposit a droplet of the non-wetting fluid on a planar solid surface immersed in the wetting fluid. The droplet stands on the surface and freely roll on it when the surface is slightly tilted.

	γ (N/m)	S (N/m)
Partial wetting		
glass-PFTS/dodecane/water	$43.2 \cdot 10^{-3}$	$-2.9 \cdot 10^{-3}$
Pseudo-partial wetting		
glass-OTS/dodecane/water	$43.2 \cdot 10^{-3}$	$2.4 \cdot 10^{-3}$
glass-OTS/dodecane/TTAB	$5.8 \cdot 10^{-3}$	$9.4 \cdot 10^{-3}$
glass-OTS/dodecane/FC-40	$5.1 \cdot 10^{-3}$	$11 \cdot 10^{-3}$
Tygon/dodecane/water	$43.2 \cdot 10^{-3}$	> 0
Complete wetting		
Tygon/dodecane/FC-40	$5.1 \cdot 10^{-3}$	> 0

Table 1: List of the system used and their properties at 25°C in the form 'solid surface/wetting phase/non-wetting phase'. TTAB stands for an aqueous solution of tetradecyltrimethylammonium bromide at 1.0×10^{-4} g/L (TTAB-I) or 4.1×10^{-3} (TTAB-II). The viscosities of the fluids are 0.89 mPa.s (all aqueous solutions), 3.4 mPa.s (FC-40) and 1.34 mPa.s (dodecane).

It is not straightforward to know a priori if a given system with $S > 0$ exhibits complete or pseudo-partial wetting. Indeed, it requires the knowledge of disjoining pressure which contains various contributions, given the complexity of the systems used (aqueous solutions of surfactants, glass surface grafted with silane). It is however rather simple to experimentally distinguish between these two types of wetting. If one deposit a drop of wetting phase on a surface immersed in the non-wetting liquids, it spreads slowly, reaching at long times a very thin film. On the contrary, we observe for the systems denoted as 'pseudo-partial' in table 1, a different behavior. The droplet spreads on the surface but reaches a steady state with a finite contact angle (see Fig. 1). Even after one week, the contact angle remains unchanged and we could thus conclude that it corresponds to an equilibrium state. Such a configuration is only expected for pseudo-partial systems where the shape of the disjoining pressure allows a coexistence between a thin wetting film and a macroscopic contact angle [3].



Figure 1: Two equilibrium states of the OTS/dodecane/water system. Left: A droplet of dodecane in water under a flat OTS-grafted glass plate exhibits a macroscopic contact angle. Right: a droplet of water in dodecane on the same surface does not stick to the surface. The droplets are about 1mm diameter in both cases.

Limiting ourselves to the van der Waals contribution to the surface interaction, we could anticipate the sign of the long range tail of disjoining pressure. It is given by the opposite of the sign of Hamaker constant of the considered system [3]. The solid surface consist of a very thin layer of silane cover-

ing a thick glass surface. For oil films much thicker than the silane layer thicknesses, the contribution from this layer could be neglected and the Hamaker constant of the system is approximated by $A_{g/o/w} = A_{g/w} - A_{w/o}$ (the indices g , o and w refers to the glass, oil and water phases, respectively). Using values from the literature [13], we find $A_{g/o/w} \approx 4.5 \times 10^{-22}$ for glass/dodecane/water (we were not able to find the value for the systems involving Tygon tubes). This positive value is consistent with our observations, since for partial and pseudo-partial systems, the interaction is repulsive at long distances, whereas it is attractive for the systems exhibiting complete wetting.

2.2. Experimental setup

The experimental setup consists in two reservoirs connected by a horizontal circular tube of radius $R = 100 \mu\text{m}$ and of length $L = 8 \text{ cm}$. It is sketched in Fig. 2. The tube is suspended in midair by drilling two small holes on each reservoir. The two reservoirs are connected to a pressure controller (Fluigent MFCS) which allows to impose a pressure difference with an accuracy of about 6 Pa. Starting from a situation where the tube is entirely filled by the wetting fluid, a meniscus is formed inside the tube by applying a pressure drop. This setup efficiently prevents the formation of droplets of the wetting fluid at the inlet of the tube: there is only one meniscus at a time in the tube. The displacement of meniscus is recorded by a camera mounted on a binocular. The meniscus velocity and its curvature are measured simultaneously, as a function of the applied pressure difference.

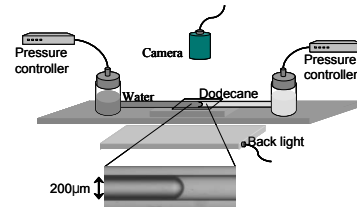


Figure 2: Scheme of the experimental setup.

3. Results

In this set of experiment, we focus on steady states. For all the results reported here, we wait until a stationary regime is reached. Although this is achieved within much less than one second in most of the tested situations, we have also observed some very long transient regimes when the velocity is very low. Special attention has been paid to do the measurement a long time after the change of pressure, and to verify that the velocity is constant during the measurement.

In steady state, the pressure difference is the sum of the capillary pressure and the viscous pressure drop corresponding to Poiseuille flow, in the region that is far from the meniscus. Due to the high aspect ratio of the tube, both end effects and the

meniscus region could be neglected so that the pressure difference is given by

$$\Delta P = -2 \frac{\gamma \cos \theta}{R} + \frac{8VL}{R^2} [\eta_1 x + \eta_2 (1 - x)] \quad (1)$$

where L is the tube length, V is the meniscus velocity, which also corresponds to the mean velocity in the tube, η_1 and η_2 are the viscosities of the two fluids, and x is the reduced position of the meniscus inside the tube. The contact angle θ is defined in the non-wetting phase. Since x is set around 0.5 and do not vary significantly during an experiment, the second term of the right-hand side could be rewritten using the mean viscosity $\bar{\eta} = (\eta_1 + \eta_2)/2$ of the two fluids. Using thereafter non-dimensional quantities defined by $\tilde{P} = \Delta P R / 2\gamma$ and $\tilde{V} = 4\bar{\eta}VL/\gamma R$, the previous equation reduces to $\tilde{P} = -\cos \theta + \tilde{V}$.

For all the systems, the capillary pressure $2\gamma/R$ lies in the range 100-1000 Pa, and the characteristic velocity $\gamma R / (4\bar{\eta}L) \approx 800 - 1.5 \cdot 10^4 \mu\text{m/s}$. Note that θ is a macroscopic contact angle, that in principle depends on the velocity for high capillary numbers ($\text{Ca} = \bar{\eta}V/\gamma$) and that could be accounted by as Cox-Voinov's law [14]. However, given the very small capillary numbers investigated in this study ($10^{-9} - 10^{-4}$), we neglect the variations of the contact angle due to hydrodynamic forces.

3.1. Partial and complete wetting

Fig. 3 shows the results obtained with the systems in complete and partial wetting. The complete wetting system exhibits a linear relation between $\tilde{V}$ and $\tilde{P}$, with a slope close to unity. Furthermore, $\tilde{V} = 0$ for $\tilde{P} \approx 1$, showing that the macroscopic contact angle remains constant and equals to 180° for receding and advancing menisci, which is confirmed by image analysis. For the partial wetting system, there are two linear branches of slope on the order of unity, but separated by a pressure interval where the velocity vanishes. The contact line is pinned in this range of pressure. When the meniscus is moving, the contact angle coincide either to the advancing contact angle or to the receding one, which is verified by the measurement of curvature shown in Fig. 3. The contact angle varies in the pinned interval to accommodate the pressure difference that is imposed. The hysteresis is rather high (90°) for this system, probably due to an inhomogeneous grafting of the surface. These two systems are thus in perfect agreement with the literature.

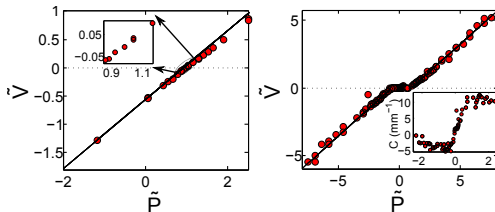


Figure 3: Left: Non-dimensional meniscus velocity in steady state as a function of the pressure drop for the tygon/dodecane/FC-40 system (complete wetting). The full lines represents $\tilde{V} = \tilde{P} - 1$. Right: PFTS/dodecane/water system (partial wetting). The slope of each linear branch is 0.81.

3.2. Pseudo-partial wetting

The meniscus velocity as a function the pressure drop obtained with the OTS/dodecane/water system is shown in Fig. 4. The results look very similar to those of the partial wetting system discussed above: two linear branches are observed for $\tilde{P} < 0.6$ and $\tilde{P} > 1$, separated by a plateau where the velocity is very small (below $10 \mu\text{m/s}$). Contrary to what we observe for partial wetting, the velocity does not strictly vanish but is very small (see the insert in Fig. 4), showing that there is no pinning. We also observe that a pressure perturbation in this regime leads to a sudden move of the meniscus with a high velocity that eventually relax after some time. These observations show that though the stationary $\tilde{V} - \tilde{P}$ relationship is at first sight similar to that of partial wetting, the responsible mechanisms for the plateau region are different. Let us recall that, for this system, $S > 0$, which means that there is always a wetting film of dodecane on the solid surface.

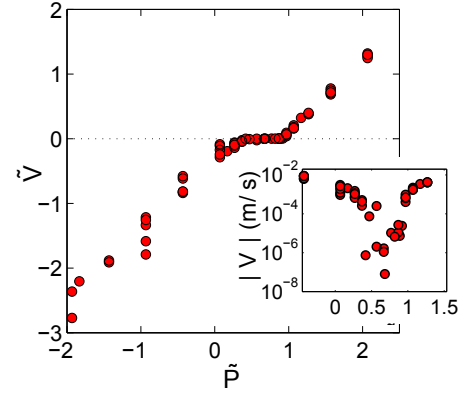


Figure 4: Meniscus velocity in steady state as function of the pressure drop for OTS/dodecane/water. The two linear branches have a slope of 1.1. Absolute values of non-vanishing velocities are shown in insert as a function of $\tilde{P}$, showing that the meniscus is not pinned but moves very slowly.

All of these observations hold for various systems. Fig. 5 displays the $\tilde{V} - \tilde{P}$ relation obtained for various aqueous solutions of standard surfactants against dodecane in OTS-grafted glass tube, together with the OTS/dodecane/FC-40 and the tygon/dodecane/water systems. All of these systems have a positive spreading parameter, and exhibit a plateau where the velocity is very small but where the contact line is not pinned. The only difference between these systems is the pressure drop at which the meniscus starts to recede with a significant velocity (receding linear branch), which is indicated in Fig. 5. It thus seems natural to relate the observation of an contact angle hysteresis-like range without pinning to the pseudo-partial nature of the wetting for all of these systems. Our experimental set up is then a method to distinguish between pseudo-partial and complete wetting conditions.

At equilibrium, the pressure is uniform inside both phases and thus $2\gamma \cos \theta_e / R = \Pi(h_e)$. Then, integrating the generalized Laplace law from the meniscus region to the flat wetting films leads to $\cos \theta_e = 1 + 1/\gamma \times \int_{h_e}^{\infty} \Pi(z) dz$, which constitute the second equation needed to define the equilibrium state [15]. Thus there is only one equilibrium contact angle expected for

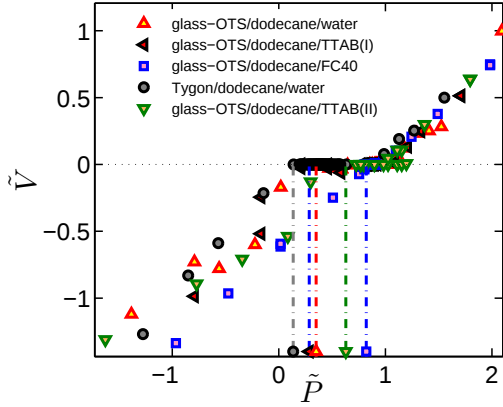


Figure 5: $\tilde{V} - \tilde{P}$ relations for various systems that have a positive spreading parameter (see table 1). The pressure corresponding to the end of the receding linear branch is highlighted by vertical dashed lines. The concentrations for the solutions of surfactants are 1×10^{-4} for TTAB(I) and 4.1×10^{-3} .

pseudo-partial wetting systems with ideal surfaces. The rigorous interpretation of the observation of pressure range where the meniscus velocity is very small for the pseudo-partial wetting systems is beyond the scope of this article. We may however think of two possible mechanisms, based either on non-ideal surfaces, either on quasi-equilibrium states.

The first possibility is to invoke topological or chemical heterogeneities of the solid surfaces which has been shown to be responsible for contact angle hysteresis in partial wetting systems. The consequences of a non-flat surface in a pseudo-partial system would however be slightly different since there is a very thin layer of the wetting phase separating the solid and the non-wetting phase. It might explain why we do not observe contact line pinning in the pseudo-partial systems, but instead a very slow movement.

The second possible interpretation relies on theoretical arguments developed by Starov and coworkers (see part 3.10 of reference [15]). They proposed that between an advancing contact angle and a receding one, the meniscus and its surrounding wetting film adopt a *quasi-equilibrium* shape which thus lead to a natural contact angle hysteresis, without surface imperfections. Due to the very small thickness of the wetting film, the equilibrium state between the infinite film far from the meniscus and the macroscopic contact angle is rather hard to achieve since any small flow in the wetting film induces an important pressure gradient. Thus, for a non-equilibrium pressure drop between the two macroscopic phases, the meniscus could reach rapidly a macroscopic contact angle which balances the applied pressure drop, leading to a very slow velocity, even though the thin wetting film is not at equilibrium. As discussed by Starov *et al.*, this quasi-equilibrium situation is greatly dependent on the disjoining pressure curve, and requires a non monotonic shape, such as in pseudo-partial cases. The advancing contact angles is expected to be close to 180° and the receding one higher than 90° , which is always the case in our observations.

4. Conclusion

Using a simple set-up, we report in this article velocity measurement of a single liquid-liquid meniscus in a tube in different wetting conditions under pressure control, and for low capillary numbers. Complete and partial wetting systems exhibit a standard behavior, that is simply accounted by Poiseuille law, and for partial wetting system, a contact angle hysteresis where the contact line is pinned. Similar experiments applied to pseudo-partial wetting systems lead to the conclusion that this type of wetting leads to an apparent contact angle hysteresis. The latter differs from the partial wetting case since the contact line is not pinned but moves very slowly. This behavior is observed for various systems and thus seems to be generic for solid-liquid-liquid systems in pseudo-partial wetting conditions.

These results ask for complementary work in order to be able to conclude on the mechanism responsible for the apparent contact angle hysteresis. We proposed two possible interpretations based either on surface heterogeneity or on the existence of quasi-equilibrium state. In particular, varying the surface roughness and measuring the disjoining pressure may help to discriminate between these two and should be the focus of future work. Finally, the meniscus dynamics in pseudo-partial wetting systems ask also for deeper observations since we notice long transient regimes before reaching the steady state described in this article.

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Chapter 4

Unstationnary dynamics

4.1 Introduction

In Chapter 3, we have focused on steady states, where the meniscus moves at a constant speed under a given pressure drop. In fact, although steady state is achieved within much less than one second in most of the tested situations, we have also observed some very long transient regimes when the velocity is very low. In this chapter, we focus on these transient regimes induced by a sudden change of the pressure drop. These regimes could be very long.

4.2 Transient regimes

With the same setup as depicted in Figure 3.2, we work with a liquid-liquid system dodecane/water inside a 200 μm -diameter OTS-silanized glass capillary tube. This system has a capillary pressure $P_c = 864$ Pa, and is in pseudo-partial wetting conditions, as discussed last chapter.

We have used the following experimental protocol to study how the meniscus displacement reaches steady state. Starting from a situation where the tube is entirely filled by the wetting fluid, a pressure drop P_i is applied to form one single meniscus inside the tube. The starting position is a few centimeters upstream from the observation field, so that the steady state regime has been reached when the measurement begins. A sudden change of pressure drop from P_i to P is made just after the meniscus enters the observation field, and the meniscus displacement is monitored. We analyze these images to get the displacement informations.

In some situations, this displacement is not linear, one of which is shown as an example in Figure 4.1. A prompt change of pressure drop from 850 Pa to 900 Pa is shown in the left part. This change leads to a very long kinetics in the position-time plot in the middle part. A high velocity is observed at the beginning and decreases markedly with time until an asymptotic constant velocity regime is reached. It takes about 0.1 s for the pressure drop to change from a stable one to another. However, it takes more than 300 s to get

a steady state regime for the meniscus velocity. This long duration response to a prompt pressure drop change is designed thereafter as the transient regime. As we could not precisely control and measure the pressure drop simultaneously, this is not a result of pressure values relaxation. It should be related to the motion of the apparent contact line.

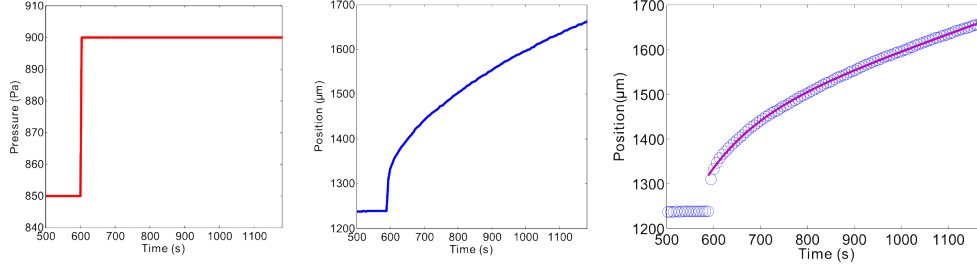


Figure 4.1: Left: a prompt ($t < 0.1$ s) step-changed pressure drop from 850 Pa to 900 Pa induces a kinetics longer than 300 s. Middle and right: the experimental and fitted relations between meniscus position $z(t)$ and time t under a system of glass-OTS/dodecane/water. (see also Figure 4.1 and Equation 4.1)

4.2.1 Characteristic time τ

The time-resolved position, shown in Figure 4.1, could be fitted by using an exponential function between meniscus position z and time t :

$$z = a \cdot e^{-\frac{t}{\tau}} + z_0 + v_{\infty} t \quad (4.1)$$

where t is the elapsed time since time t_0 , which is the moment of the pressure drop step, z_0 is the meniscus position at t_0 , V_{∞} is the final steady state velocity at $t = \infty$. A fitted curve is sketched in Figure 4.1 with two fitted parameters $\tau=108.8$ s and $V_{\infty}=0.4$ $\mu\text{m/s}$. The blue solid curve corresponds to the exponential fit. We focus on the measurement of the characteristic time, which exhibits big variations as a function of the applied parameters, and in particular the final pressure drop.

We vary the initial pressure P_i and final pressure P between -1 kPa and 2 kPa and observe in every cases an exponential relaxation. Some examples of transient regimes are shown in Figure 4.2, 4.3 and 4.4.

Independently of the displacement directions, the transient regimes occur either between two advancing displacements, or two receding displacements, or between one advancing and one receding displacements. The transient regimes that follow the pressure drop step could be very long or very quick. Distinguished from the duration of the transient regimes, we made a rough classification by characteristic time τ :

- (1) Fast transient regime ($\tau < 2$ s). In Figure 4.2, every figure has two steady displacements without transient regimes. The velocities of each steady displacement could be measured by their slopes. Their displacements give representative directions:

from advancing ($90 \mu\text{m/s}$) to advancing ($1703 \mu\text{m/s}$), from receding ($-718 \mu\text{m/s}$) to receding ($-14041 \mu\text{m/s}$), from receding ($-109 \mu\text{m/s}$) to advancing ($2218 \mu\text{m/s}$). All the three have final velocities relatively high.

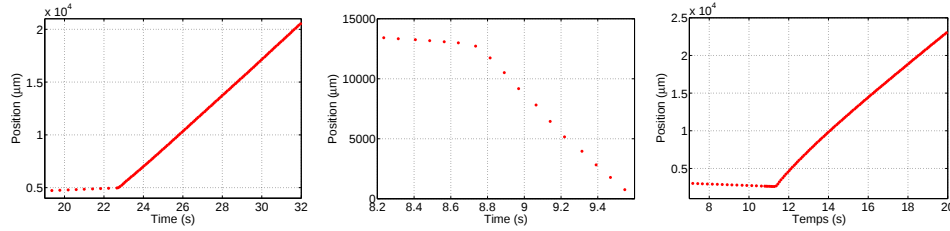


Figure 4.2: Three examples of fast transient regimes: 950 Pa $\rightarrow$ 1150 Pa, 550 Pa $\rightarrow$ -850 Pa, 550 Pa $\rightarrow$ 1150 Pa under a system of glass-OTS/dodecane/water.

- (2) Long transient regime ($\tau < 50$ s). In Figure 4.3, every figure has two steady displacements and a transient regime. The characterized time τ of transient regimes and velocities V_∞ of the second displacements could be fitted by Equation 4.1. We get $\tau = 2.5$ s, 5.2 s, 31.3 s and $V_\infty = -845 \mu\text{m/s}$, $912 \mu\text{m/s}$, $10.4 \mu\text{m/s}$, respectively. We find the final velocities smaller than those of the fast transient regime.

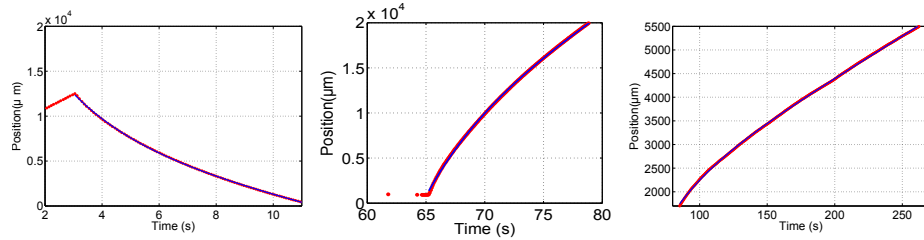


Figure 4.3: Three examples of long transient regimes: 1150 Pa $\rightarrow$ 650 Pa, 550 Pa $\rightarrow$ 750 Pa, 850 Pa $\rightarrow$ 950 Pa under system of glass-OTS/dodecane/water.

- (3) Very long transient regime ($\tau > 50$ s). In Figure 4.4, every figure has two steady displacements and a transient regime. The characterized time τ of transient regimes and velocities V_∞ of the second displacements could be fitted by Equation 4.1. We get $\tau = 5544$ s, 51.7 s, 87.2 s, respectively. The meniscus decelerates and the final velocities are not zero.

Several displacements with very long transient regimes are recorded during quite long periods, and the final velocities are stable. One of them is shown in Figure 3.7, a steady state velocity of $V = 90 \text{ nm/s}$ leads to a displacement of 4.5 mm during about 17 hours. This special transient property seems to be related with small velocities.

Note that the fact that the velocities are small but non vanishing together with the presence of transient regimes demonstrate that there is no strong pinning of the contact line in these systems.

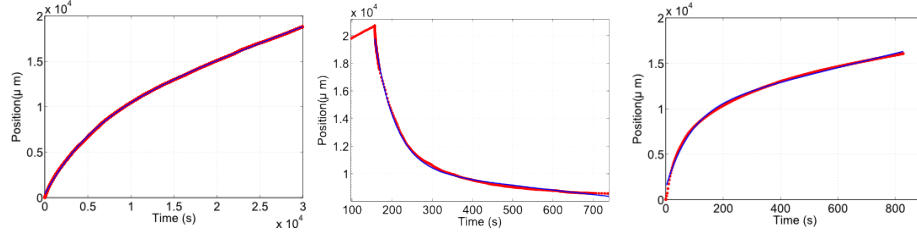


Figure 4.4: Three examples of very long transient regimes: 800 Pa→850 Pa, 950 Pa→750 Pa, 850 Pa→900 Pa with $\tau = 5544$ s, 51.7 s, 87.2 s under system of glass-OTS/dodecane/water.

4.2.2 Pressure drop diagram

For this given system, the relaxation times of menisci are studied as a function of two parameters: the initial and arrival pressure drops P_i , P . We want to study the influence of these two pressures drops on the characteristic time of the transient regime.

Menisci displacements are observed for several series of pressure drop step, $P_i = 550$ Pa, 850 Pa, 950 Pa and 1150 Pa. For each P_i , several final pressures P are tested. The characteristic times τ are obtained by fitting the transient response by Equation 4.1. We observe very different characteristic times, from below 1s to several hours. We use the above detailed classification of the transient times to map the observation on a diagram in the $P_i - P$ space parameter. It is shown in Figure 4.5 where the black point($\cdot$), blue star($*$) and red circle($\circ$) design the fast, long and very long transient regimes.

Several general trends could be drawn from this diagram:

- The transient regimes are symmetrical in the vicinity of P_c .
- The transient regimes depend only on the arrival pressure drop P , and does not depend much on P_i .
- The very long transitions occur around P_c .

4.2.3 Correlation with the steady state velocity V_∞

As suggested by the above rough analysis, τ does not seem to depend on P_i . In Figure 4.6, we thus plot τ as a function of arrival pressure drop P . The characteristic time τ presents a huge increase around the capillary pressure P_c . The pressure range where the characteristic time is rather high corresponds to the so-called plateau regime (or hysteresis zone) observed in the steady state.

Figure 4.6 presents an empiric correlation between the characteristic time τ in the transient regime and the (unsigned) steady state velocity. Both quantities seem to be quite well correlated given the precision and the reproducibility of the experiment, and the characteristic increases linearly with respect to the inverse of the steady state velocity. All

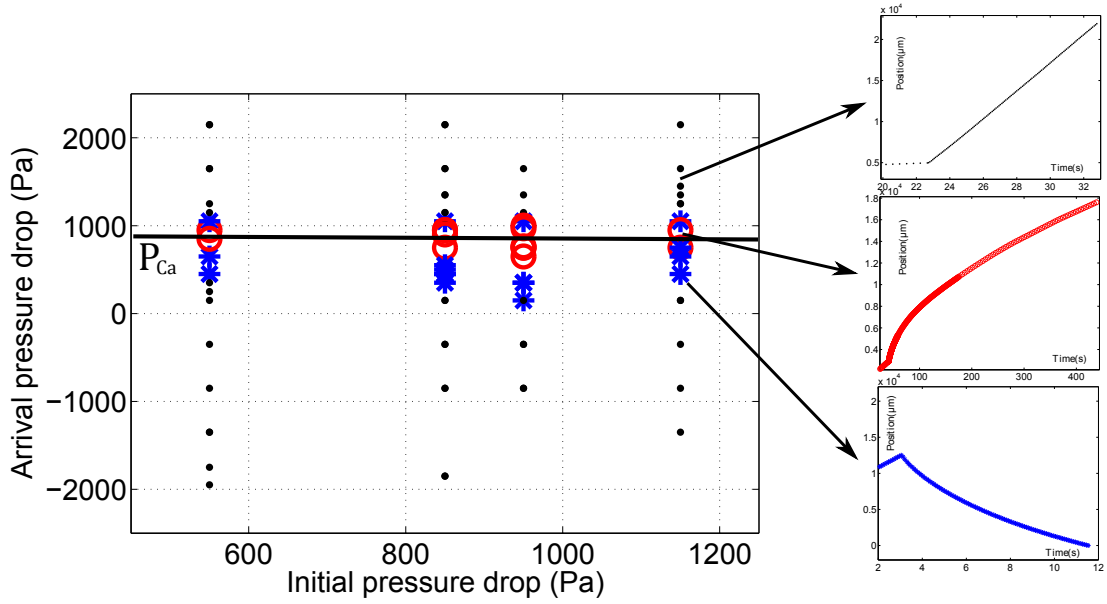


Figure 4.5: Diagram showing the couples (P_i, P) that have been investigated for the system glass-OTS/dodecane/water. Each experiment is classified according to its characteristic time (see text for details): fast transition ($t < 2$ s, dots), long transition ($t < 50$ s, stars), very long transition ($t > 50$ s, circles).

types of the transient regime agree well with this linear relation. It suggests that τ is in a very first approximation roughly proportional to $1/v_\infty$.

$$\tau = \frac{L}{v_\infty} \quad (4.2)$$

with a length scale, which would be defined by this relation, on the order of 2 mm.

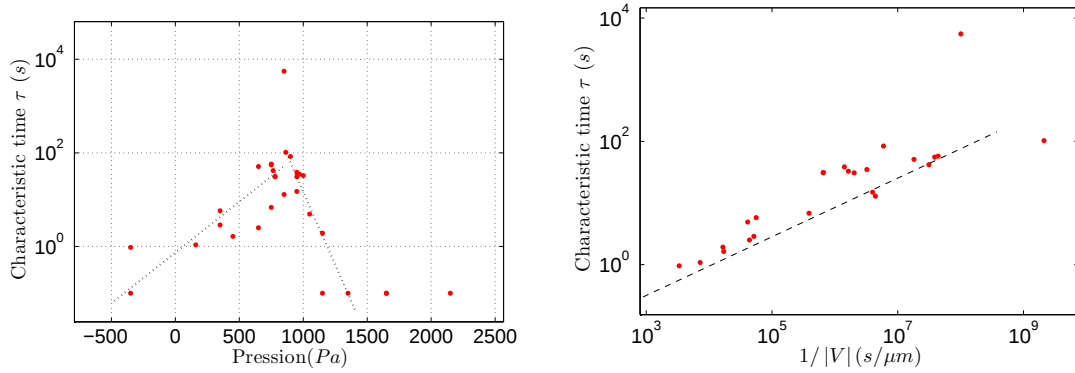


Figure 4.6: Characteristic time $\tau(\cdot)$ as a function of the arrival pressure P (Left), together with the inverse of the velocity in the steady state l/V_∞ ($\diamond$), with $l = 2$ mm (Right).

4.2.4 Transient regimes in other systems

Transient regimes occur also in other couples of liquids. Here we show a simple table of all the studied solid/liquid/liquid systems. The existence of transient regimes may be a criterion to distinguish the wetting property of a system. Table. 4.1 shows the properties of certain systems. Complete wetting is easy to distinguish from others without the transient regime and hysteresis plateau. The discussed pseudo-partial wetting has this property of very long transient regimes except one system: glass-OTS/dodecane/FC-40. This system has a quite short hysteresis-like plateau, but the transient regimes are all quite short or nearly $\tau = 0$. We note that the partial systems do not exhibit long transient regimes but remain pinned inside the hysteresis zone. This dynamic property seems thus to be a consequence of the wetting film. We believe that the transient regime is the period throughout that the macroscopic meniscus and the microscopic wetting films are coordinating their values. This could involved a change of contact angle θ and thickness h . The steady displacement follows this transition. θ and h have reached their equilibrium values, that are the values of the final steady states V_∞ .

	Transient regime	Hysteresis plateau	Wetting property
glass-OTS/dodecane/water	Yes	Yes	pseudo-partial
glass-OTS/dodecane/dyed water	Yes	Yes	pseudo-partial
glass-OTS/dodecane/TTAB	Yes	Yes	pseudo-partial
glass-OTS/dodecane/CTAB	Yes	Yes	pseudo-partial
tygon/dodecane/water	Yes	Yes	pseudo-partial
galss/dodecane/water	No	Yes	Partial
galss-PFTS/dodecane/water	No	Yes	Partial
glass-OTS/dodecane/FC-40	No	Yes	pseudo-partial
tygon/dodecane/FC-40	No	No	complete

Table 4.1: All the studied systems are shown with their properties of hysteresis plateau, transient regime and wetting types. These properties could also be a method to distinguish the wetting types. The systems with long transient regimes and hysteresis plateau are pseudo-partial wetting. The glass-OTS/dodecane/FC-40 has not transient regimes but $V \neq 0$ hysteresis. It's also distinguished as pseudo-partial wetting. The systems with $V = 0$ hysteresis plateau are partial wetting. The systems without transient regimes and hysteresis plateau are in complete wetting situation.

4.3 Discussion

The very huge time scales that we have reported above are rather puzzling. They exists only around the hysteresis zone, for system in pseudo-partial wetting conditions. The less the steady state velocity, the higher the relaxation time. When the corresponding steady

state is very close to the equilibrium contact angle, then the characteristic time could be as high as 10^3 s. From an experimental point of view, this result ask for a precise protocol. In order to measure the steady state velocity, it is necessary to wait a great amount of time in the hysteresis zone. This is why we have used for the experiments in steady state (see previous chapter) such a precise protocol. If the pressure is changed during the transient regime, then meniscus displacement is very hard to understand and reproducibility is difficult to ensure. It seems that the meniscus movement is governed by the history of the pressure variations. This issue is rather consistent with the very long transient times reported in this chapter.

Similar transient regimes has also observed occasionally in other systems. With a water/cyclohexane system, Chertcoff [108] *et al.* have studied the meniscus dynamics in a millimeter-size glass capillary tube initially saturated with cyclohexane, which is water wet. Their setup is very similar to the one we have used, since the meniscus movement is controlled by a pressure difference. After a sudden change of pressure, they report transient regimes of characteristic time that could be as high as a few hundreds of seconds. These effects are particularly strong at very low capillary numbers between 3×10^{-9} and 5×10^{-7} . It seems that these observations is very similar to ours, but unfortunately, the authors do not precise the exact type of wetting of their system. Given the fact that we have only seen these kinds of transient regimes in pseudo-partial wetting conditions, it is temptative to think that the systems they used is also in pseudo-partial wetting conditions. The authors suggest that the relaxation are due to adsorption sites with a wide range of characteristic times: decreasing the velocity increases the number of sites active for adsorption and enhances the wetting of high-energy glass surface by water. However, such an interpretation do not really explain why there exists a transient regime at a very low capillary numbers.

The long times found suggest that the small thickness of the wetting films play a great role, since flows in these films are small. However, an hydrodynamics approach (see Section 1.4.2) would predict that the film thickness is monotonically slightly changed in pseudo-partial wetting systems, when the pressure is varied around the equilibrium contact angle. This type of approach would thus not lead to a maximum of characteristic times at the equilibrium contact angle. Moreover, it could probably not explain the symmetry we found around the equilibrium. If the pressure is above or below the equilibrium pressure, we indeed find that the velocity is high at time zero and then relaxes. It seems thus that the distance to equilibrium is the key to the observed relaxation.

We found an empiric correlation between the velocity in the steady state and the characteristic time. Their ratio is constant and equals 2 mm. This length is much higher than channel size, but we are not able to provide any satisfying interpretation of the physical meaning of this length scale.

Our data in the steady state are rather compatible to a motion of the contact line controlled by thermally activated depinning events. It might be interesting to extend that kind of mechanism to the out of equilibrium case. Yet, such a description is not available in the literature, and ask for theoretical work, maybe using out-of-equilibrium statistiscal mechanics.

4.4 Conclusion

We report in this part some striking observation of the contact line movement after a sudden change of pressure in the hysteresis zone, for pseudo-partial wetting systems. Its velocity is much higher just after this change than the steady state velocity. It then relaxes to the steady state value with a characteristic time that greatly depends on the velocity in the steady state. It is very high close to the equilibrium and we found that it varies proportionally to the inverse of the steady state velocity.

These results ask for some interpretations. Since it occurs only in pseudo-partial wetting system, inside the hysteresis controlled by depinning events, the corresponding mechanism should involve the small thickness of the wetting films that are presented in pseudo-partial systems, and the surface roughness is responsible to the hysteresis.

Although the interpretations are not very clear yet and ask for theoretical work, these results do have strong experimental consequences. In order to be able to measure steady state velocities, it is necessary to wait until the end of the transient regime. Since the characteristic times are in the hysteresis zone on the order of 100 s, protocols should be defined with great attention. Very complex contact line movements could be observed if one does not wait enough before changing the pressure.

4.5 Summary

Transient regimes

- A very long kinetics occurs when a prompt change (about 0.1 s) of pressure drop is applied. A high velocity is generated and decreases markedly with time until an asymptotic, constant velocity regime is reached. It may take more than several hundreds of seconds to get a steady state velocity.
- Characterized time τ describes the long relaxation of velocity. It is fitted by an exponential function.
- By varying the initial and arrival pressure drop, the characterized time displays various relaxation durations from 0 s to 10^4 s. Three types of transient regimes are distinguished by τ and displayed in the parameter plane initial and arrival pressure drops.
- The transient regimes are symmetrical in the vicinity of capillary pressure P_{Ca} . The transient regimes depend only on the arrival pressure drop P , and does not depend much on P_i . The very long transient regimes occur for final pressure drops around P_{Ca} .
- The characteristic time τ presents a logarithmic trend at both sides of capillary pressure P_{Ca} . τ is roughly proportional to $1/V_\infty$. They define a length scale of $L = 2$ mm.

Part III

Flows in corner films

Chapter 5

Corner flow around a static meniscus

5.1 Introduction

The movement of a liquid-liquid meniscus in a circular tube at small capillary numbers is a rather simple problem since it follows Poiseuille's law with an effective pressure that incorporates the capillary pressure. However, for a tube of arbitrary cross-section exhibiting sharp corners, which are useful example of simple pore shapes, capillarity requires that the wetting liquid remains along the corners. These corner films may flow.

In this part we experimentally investigate the role of these corner flows on the dynamics of a liquid-liquid meniscus, under complete wetting situation, by taking advantage of a microfluidic PDMS cross-junction. A diagram of coupling pressure drops under stationary state is in Chapter 5.

5.1.1 Corner flow

The spreading of wetting liquids with a liquid or air ambiance in a capillary tube is a basic problem. Its spreading rate depends on the fluid properties (interfacial tension, viscosity, wetting) and substrate properties (roughness, interaction with liquid: van der Waals, disjoining pressure...) [13]. It was shown, both theoretically [109] and experimentally [34], that a complete wetting liquid is solely controlled by the drops in the capillary and hydrostatic pressures in the macroscopic liquid body. Under conditions of strong preferential wetting, the emphasis has been placed on the transport of the wetting phase by flow in surface grooves and edges, in which is often called a "wetting film", and on the snap-off of threads of the non-wetting phase, which is caused by capillary instabilities that occur because of the presence of the wetting film on the pore walls. There are many studies of capillary driven flow in a cylindrical tube [110] and in the irregular section channels [111]. In a quasi-static displacement and in a displacement at very low capillary number in the order of 10^{-7} , the movement of the wetting phase plays a major role in the displacement process.

Three or two phases flow (nonaqueous phase liquid, water, gas) in microchannels are discussed for oil recovery [112–115]. In a polygonal capillary, static menisci are governed

by the Young-Laplace equation, which expresses in differential form the force balance between interfacial tension and the net pressure force acting on an element of the meniscus, *e.g.* imbibition and drying of a liquid/air meniscus. Due to capillary forces, the size and movement of air-liquid meniscus along an interior corner of a container is studied theoretically and experimentally [116], or in capillary tube with irregular sections: square ones [117–119] and triangle ones [118, 120, 121]. Dong and Chatzis [117] have shown, theoretically and experimentally, the imbibition rate of a wetting liquid in the corners of a square capillary tube occupied predominantly by the non-wetting gas phase. The velocity of imbibition depends on the fluid properties (interfacial tension, viscosity), the contact angle, and the geometry of the corner, as characterized by the tube size and the degree of roundedness.

Usually capillary number, roughness of the microscopic tubes and shape of cross section play an important role during imbibition [122, 123]. As triangles provide a useful example of simple pore shapes, the exact meniscus curvature of perfectly liquid draining from pores of general triangular cross section is calculated [124]. An interacting triangular tube bundle model is developed, which is consistent with the experimental results of non-wetting fluid trapping in another wetting fluid in porous media [125].

Numerical simulations have shown the meniscus shapes in irregular section tubes in three dimensions [47, 126, 127] or two [128]. Numerical results computed from the augmented Young-Laplace equation has an excellent agreement with a profile of an air-liquid meniscus in a square capillary [47]. Furthermore, theoretical models of relationship between fluid configuration and Capillary number (or flow rate) are built for air-liquid imbibition in a square capillary [123].

The movement of a solid/liquid/liquid contact line has been studied since 1970's [129]. Experimental results investigate the mechanisms of this displacements of one fluid by another in a network of capillary ducts [5]. The meniscus in Figure 5.1 is coexist with the wetting fluid remaining in the extreme corners of the cross-section.

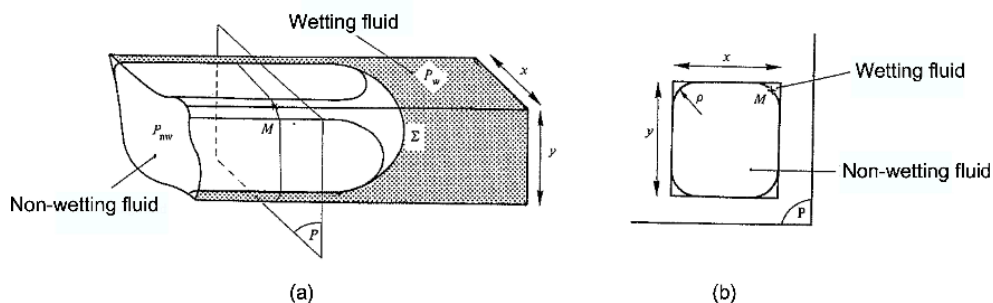


Figure 5.1: Situation of the fluids in the section of a duct with pressures P_w in wetting fluid and P_{nw} in non-wetting fluid [5]. (a) perspective view, (b) sectional view.

Controlling the flow patterns between two immiscible phases in microchannels has attracted a lot of attentions. Droplet formation has been widely studied in various microgeometries. Well structured flow patterns (drops, pears, pearl necklaces, ...) are generated by

two-phase flows in immiscible fluids through hydrodynamic focusing in square microchannels [130, 131]. This crossed microchannel could generate droplets with a high degree of monodispersity [132, 133]. Generally, the continuous phase wets the walls well. The fluid interaction with the walls plays an important role for the flow pattern formation. The wetting property of liquids on the substrate leads to different regimes [130]. The modification of droplets velocity by the crossed channels is studied [134].

During these processes, the wetting fluid can flow along the edges of the ducts. Meniscus dynamics are studied strongly on the indirect control of corner flows in a microchannel. But direct controls are not discussed yet.

5.2 Experimental approach

5.2.1 Wetting properties of using systems

We study the displacement of Fluorinert oil FC-40 in a straight PMDS microfluidic channel filled with silicone oil V20. Figure 5.2 displays the velocity of the meniscus as a function of the pressure drop. The velocity is proportional to the pressure drop. There's no contact angle change between advancing and receding situation and no pressure plateau region for velocity $v = 0$. It means that the meniscus could advance or recede without changing curvature, which demonstrates a complete wetting situation. Further, the slope is 1.2×10^{-8} corresponds to hydrodynamic resistance R_h . The x-intercept 220 Pa corresponds to the capillary pressure $P_{Ca} = 237$ Pa. These measurements are in agreement with the spreading parameter value S , which is positive and the Hamaker constant which is negative.

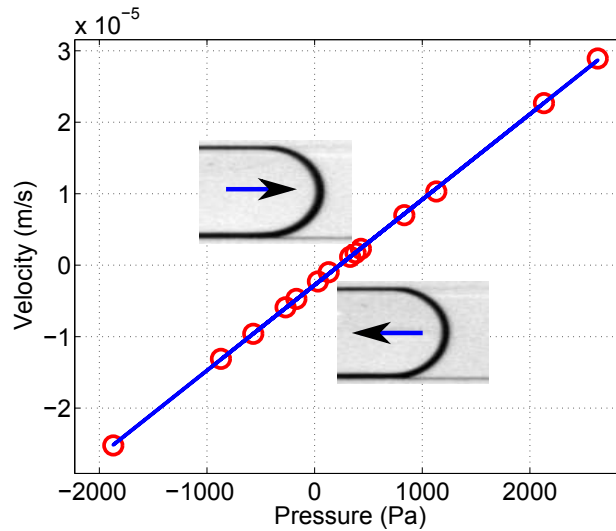


Figure 5.2: A velocity-pressure relation checks the complete wetting system: Fluorinert oil FC-40/silicone oil V20/PDMS. Straight PDMS channel has a cross section of $50 \times 200 \mu\text{m}$.

Complete wetting	γ (N/m)	S (N/m)	A
PDMS/Dodecane/FC-40	4.7×10^{-3}	7.99×10^{-3}	-5.2×10^{-24}
PDMS/Silicone oil V20/FC-40	5.1×10^{-3}	2.56×10^{-3}	-1.4×10^{-22}
PDMS/Silicone oil V5/FC-72	2.8×10^{-3}	4.41×10^{-3}	-1.9×10^{-23}

Table 5.1: List of the used complete wetting system and their properties at 25° in the form 'solid surface/wetting phase/non-wetting phase'.

5.2.2 Setup

We want to control the displacement of a meniscus. In order to control the flow of both phases, we need to set the pressure drop in the non wetting fluid but also in the wetting fluid. In order to do so, we focus on a cross geometry (see Figure 5.3). It consists of two channels: main one with width $w_1 = 50 \mu m$, length $L_1 = 12 mm$, and crossed one with $w_2 = 20 \mu m$, $L_2 = 100 \mu m$, which has each side a prolongation with width $w = 200 \mu m$, $L_3 = 3 mm$. In these crossed channels, three pressures P_1 , P_2 and P_3 could be applied at four ends to control the meniscus and the corner flows..

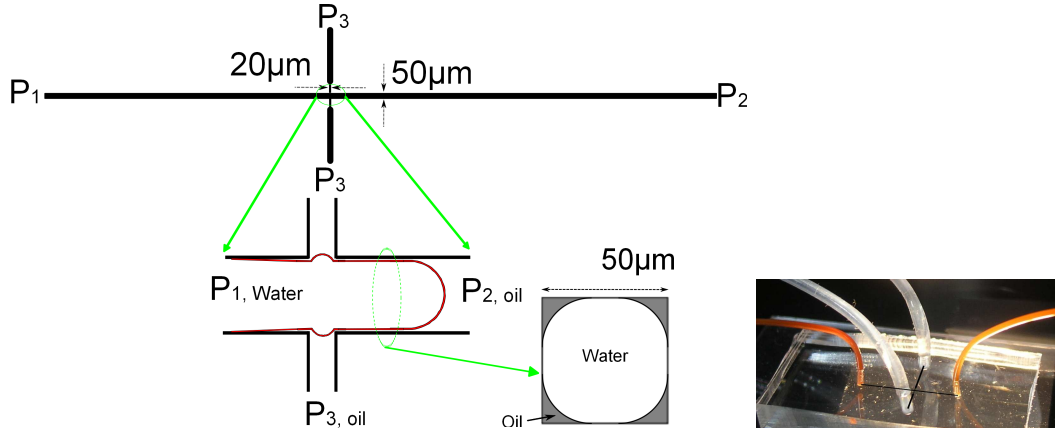


Figure 5.3: Upper part is the schematic design of microchannels. Zoom of junction zone and sectional view of the rectangular channel.

By a procedure of photolithography and PDMS molding, the height of channels is well controlled $h = 50 \mu m$. The capillary pressures, which keep the meniscus a constant contact angle θ , are in main channel: $P_{Ca1} = \gamma(2/w_1 + 2/h)$ and in crossed channel: $P_{Ca2} = \gamma(2/w_2 + 2/h)$.

The inlet of the main channel is connected to a reservoir filled with fluorinated oil FC-40. This reservoir bears a pressure P_1 . The outlet is connected to a reservoir filled with silicone oil. This reservoir bears a pressure P_2 . The two inlets of the perpendicular channels are connected to a reservoir filled with silicone oil. In this last reservoir the pressure is equal to P_3 . All three reservoirs are connected with a pressure controller (Fluigent MFCS 4C) which allows to impose pressures P_1 , P_2 and P_3 with an accuracy of about $6 Pa$ in a range lying between 0 and $2500 Pa$.

5.2.3 Method

To be sure to apply a given pressure drop on the liquid-liquid meniscus, we must avoid the formation of droplets or bubbles in the channels or in the connexions.

Once the chip is connected with reservoirs through tubes, a pressure drop is applied to push the preferentially wetting liquid until the channels are filled by wetting fluid. Starting from this situation, another pressure drop is applied to form one single meniscus (before the junction) in the channel by applying a set of pressure drops with great care.

$$P_{12} = P_1 - P_2, \quad P_{32} = P_3 - P_2 \quad (5.1)$$

We restrict our study to a limited range of pressure drop in order to avoid the formation of drops at the junction. P_{12} is slightly above the capillary pressure $P_{Ca} = \gamma(2/w_1 + 2/h)$ and P_{32} remains closed to zero. The displacement of meniscus is recorded by a camera *AVT Pike F505B* mounted on a binocular *Olympus SZX16*. The meniscus velocity and sectional flow shapes are measured simultaneously, as a function of the applied pressure drops. We experimentally investigate the role of corner flows on the dynamics of a liquid-liquid meniscus. The corner flows are controlled under a pressure drop through wetting liquid in the corners.

5.2.4 Pressure drop limitation

As we have mentioned, the applied pressure drops should be in a limited range, which is between two regimes: drop forming and invasion in crossed channels, as sketched in Figure 5.4. The left one shows the pressure limit when the drops begin to be formed. The right one shows the pressure limit when the wetting liquid invades in the crossed channels.

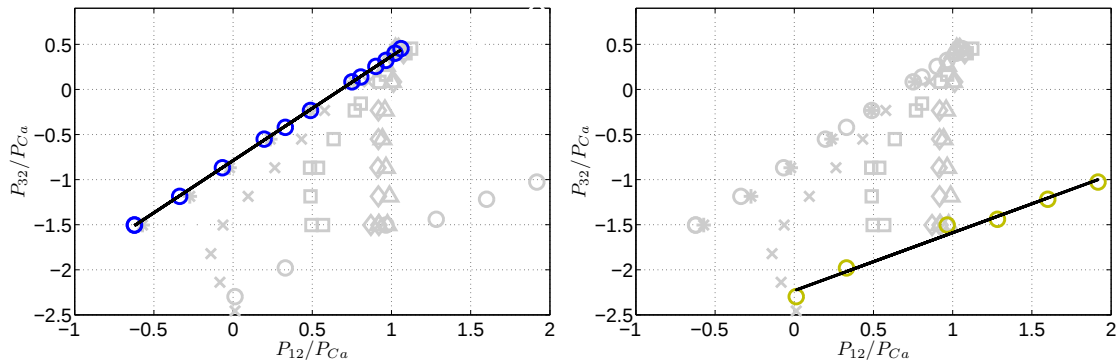


Figure 5.4: The limits of pressures drops. Left: the pressure limit when the drops begin to be formed. Right: pressure limit when the wetting liquid will invade in the crossed channels.

In the following, we restrict our study to the pressure drop values under which the meniscus remains in the main channel.

5.2.5 Corner flow illustration of confocal microscopy

As the pressure drops are applied to control the two phase flows, we would like to observe their velocity fields. Confocal microscopy is a good method to probe these corner flows.

5.2.5.1 Principle of confocal microscopy

Confocal microscopy is an optical imaging technique used to reduce the optical depth and contrast of a micrograph by using point illumination and a spatial pinhole to eliminate out-of-focus light in specimens that are thicker than the focal plane [135]. It enables the reconstruction of three-dimensional structures from the obtained images. This technique has gained popularity in the scientific and industrial communities and typical applications are in life sciences, semiconductor inspection and materials science.

The principle of confocal microscopy is sketched in Figure 5.5. The confocal principle in epi-fluorescence laser scanning microscopy is presented in the left part. Coherent light emitted by the laser system (excitation source) passes through a pinhole aperture that is situated in a conjugate plane (confocal) with a scanning point on the specimen and a second pinhole aperture positioned in front of the detector (a photomultiplier tube). As the laser is reflected by a dichromatic mirror and scanned across the specimen in a defined focal plane, secondary fluorescence emitted from points on the specimen (in the same focal plane) pass back through the dichromatic mirror and are focused as a confocal point at the detector pinhole aperture.

The significant amount of fluorescence emission that occurs at points above and below the objective focal plane is not confocal with the pinhole and forms extended airy disks in the aperture plane. Because only a small fraction of the out-of-focus fluorescence emission is delivered through the pinhole aperture, most of this extraneous light is not detected by the photomultiplier and does not contribute to the resulting image. The dichromatic mirror, barrier filter, and excitation and emission points on a specimen to a new plane that becomes confocal with the pinhole apertures of the light source and detector.

As only one point in the sample is illuminated at a time, 2D or 3D imaging requires scanning over a regular raster (*i.e.*, a rectangular pattern of parallel scanning lines) in the specimen. The achievable thickness of the focal plane is defined mostly by the wavelength of the used light divided by the numerical aperture of the objective lens, but also by the optical properties of the specimen. The thin optical sectioning makes these types of microscopes particularly good at 3D imaging and surface profiling of samples.

We use a confocal microscope of *CARL ZEISS LSM 5 LIVE*. With the tracers "fluorescent microspheres", which consists of 1 μm polystyrene beads loaded with fluorescent dyes commercialized by *Molecular Probes*, we choose the laser at wavelength 488 nm and a filter of *LP505*, which passes the wavelength higher than 505 nm to the detector. And for our channel of width 100 μm , an objective of *EC40 $\times$* with adapted index $n = 1.30$ is utilized, which is mounted on a piezo stage from *Physik Instrumente*, which allows us to construct 3D imaging by scanning the different focus plane of z direction with an accuracy of 0.9 $\mu\text{m}/\text{layer}$. We scan the several horizontal planes in the channels. The scanning is

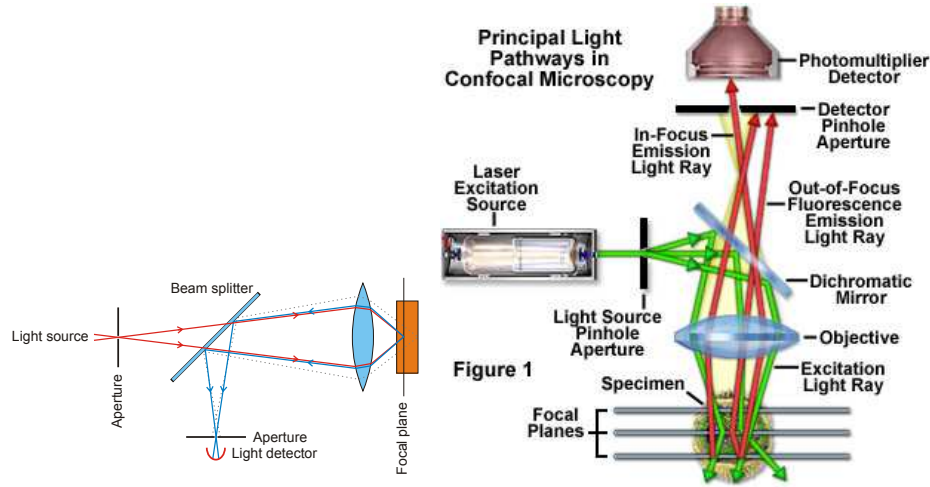


Figure 5.5: schematic drawing of confocal microscopy.

piloted by a software *zen10*. And the velocity fields are analyzed by tracking the particles trips with a home-made MATLAB program of Hugues Bodiguel.

5.2.5.2 Reverse flow

Here, Figure 5.6 shows an illustration of the velocity fields of a system with an aqueous phase FluoSphere/TTAB/Water/Glycerin (with a ratio on mass of 0.7% : 0.3% : 40% : 59%) and an oil phase dodecane in PDMS microfluidic chip. The chip is designed as Figure 5.3, and the meniscus control is described in the section 5.2.3. Two pressure drops P_{12} and P_{32} have the opposite signs, so two reverse flows are shown in two layers: one near the channel wall and another in the middle. The white points correspond to the particles and the green flashes correspond to the directions and magnitudes of velocities of these particles. The Poiseuille flow in the left part shows no influence of the corner oil flows on the central aqueous phase. The right one shows a strong reverse flow near the channel wall and low velocities in the center.

5.3 Diagram of pressure drops

We study the displacement of a meniscus between fluorinated oil FC-40 and silicone oil V5. Once the meniscus has moved as shown in below part of Figure 5.3, the meniscus dynamics is a result of local pressure drops. To study these effects, we measure the pressures which make the meniscus velocity $v = 0$ at a position L .

This stationary state corresponds to one only pressure drop, and even a small disturbance could displace the meniscus. Applied pressure drop advances the meniscus when it is bigger than P_{Ca} , in the contrary, the meniscus recedes. To simplify the measurements we need to define an almost stationary state ($v \cong 0$): when a meniscus is displaced less than

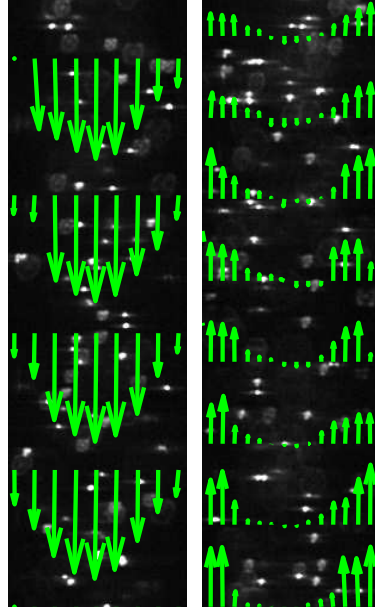


Figure 5.6: Illustration of reverse flow in the PDMS chip with crossed channels. With the system FluoSphere/TTAB/water/glycerin and dodecane in PDMS, the channel has a section of $100 \times 50 \mu m$, in a position of $100 \mu m$ from the cross. Each photo has a width of $100 \mu m$. They have heights of $h_{left} = 5 \mu m$, $h_{right} = 19.5 \mu m$ for the two layers.

$5 \mu m$ during a period of 300 seconds under stationary pressures drops. This approximation gives a criterion to measure local pressure which is almost equal the capillary pressure. We study the meniscus dynamics for different positions: before, far from and near the junction.

5.3.1 Meniscus before and far after the junction

5.3.1.1 Single channel

If we consider a general situation: the movement of a liquid-liquid meniscus in a single capillary. Its dynamics is dominated by local pressure drops around the meniscus as shown in Figure 5.7. In equilibrium, we have $P_1^* - P_2^* = P_{Ca}$, which makes the meniscus with velocity $v = 0$. These effective pressures P_1^* , P_2^* could be reduced for any meniscus.

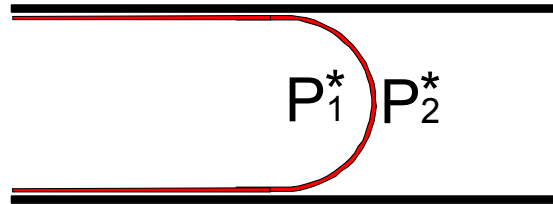


Figure 5.7: Dynamics of the meniscus could be dominated by the effective pressures drop around the meniscus.

5.3.1.2 Before the junction

Near a junction, effective pressure P_2^* could be changed by a wetting liquid flow between pressure P_2 and P_3 . For a meniscus after the junction, corner flows could complicate the pressure distribution. We begin with a situation without the corner flow when the meniscus is before the junction.

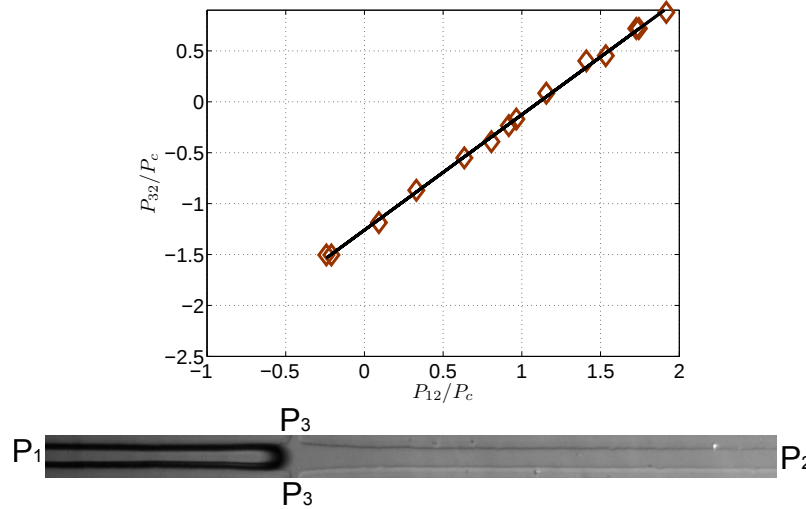


Figure 5.8: A linear relation for a meniscus before the junction. The slope is 1.12.

For a given position before the junction, we search a pressure drop P_{32} for a given P_{12} which leads to an almost stationary state *i.e.* no displacement of the meniscus. A series of P_{32} are measured, which corresponds to a series of P_{12} . We find that a couple of pressure drops could stabilize the meniscus at a given position. For a meniscus position shown in lower part of Figure 5.8, we have couples of pressure drops, which stabilize the meniscus at this position. These pressure drops are normalized by capillary pressure P_{Ca} and drawn in Figure 5.8. This linear relationship with a slope of 1.12 means a linear distribution of these two pressure drops P_{12} and P_{32} . Normalized by capillary pressure P_{Ca} , the pressure drop graphics show a direct comparison with P_{Ca} . This pressure drops relation could also be compared easily with systems with different interfacial tensions or channel geometries.

Other linear relations are observed for different positions before the junction, which are parallel lines with the curve in Figure 5.8. They show a pressure change in the wetting phase related to the distance L , which is not the key point to study here.

5.3.1.3 Far after the junction

Now we focus on situations where the nose of non-wetting liquid has a length L after the cross junction. When L is as big as shown in the lower part of Figure 5.9, the couples of pressure drops which lead to an almost stationary state are shown in the upper part. These points show that the meniscus advances ($v > 0$) when P_{12} is bigger than the capillary

pressure and recedes ($v < 0$) when P_{12} is smaller than the laplace pressure. These points are independent with P_{32} , which means there is no influence of corner flows.

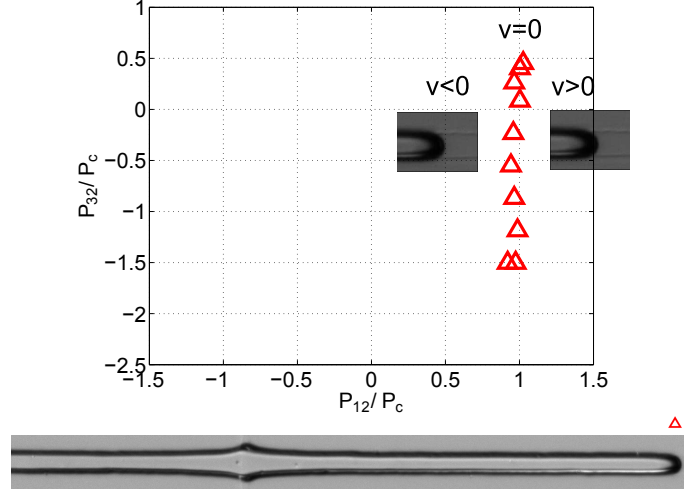


Figure 5.9: A linear relation for a meniscus at a distance of $L = 15.4 \cdot w$, where w is the channel width. The two sides of this curve lead to an advancing or receding meniscus until a new equilibrium.

5.3.2 Diagram of pressure drops

Now we focus on the nose of non-wetting liquid has a length L after the cross junction. We measure the couples of pressure drops which stabilize the meniscus at other positions. They are shown in Figure 5.10, with positions $L = 0, 0.2 \cdot w, w, 1.8 \cdot w$ and $5.8 \cdot w$, where w is the main channel width. Each series has its own symbol. These series of pressures for various positions form a diagram, which indicates the movement of meniscus under a couple of pressure drop for a position near the junction. By applying a set of pressures in the diagram, a moving meniscus with quite small velocity could decelerate until an almost stationary state at a given position.

From this diagram, we can conclude the following trends:

- The curve with $L = 15.4 \cdot w$ illustrates the situation where $L \rightarrow \infty$. There is almost no influence of corner flows.
- The curve with $L = 0$ shows another situation when there are no corner flows.
- The curves with $L = w$ and $1.8 \cdot w$ have a turn when P_{32} is small. It is the result of combination of pressure drops and corner shapes, which will be discussed in the hydrodynamic resistance model.

Two other complete wetting systems are also studied: FC-40/silicone oil V20 and FC-72/silicone oil V5 with PDMS. We get the same behavior as sketched in Figure 5.11.

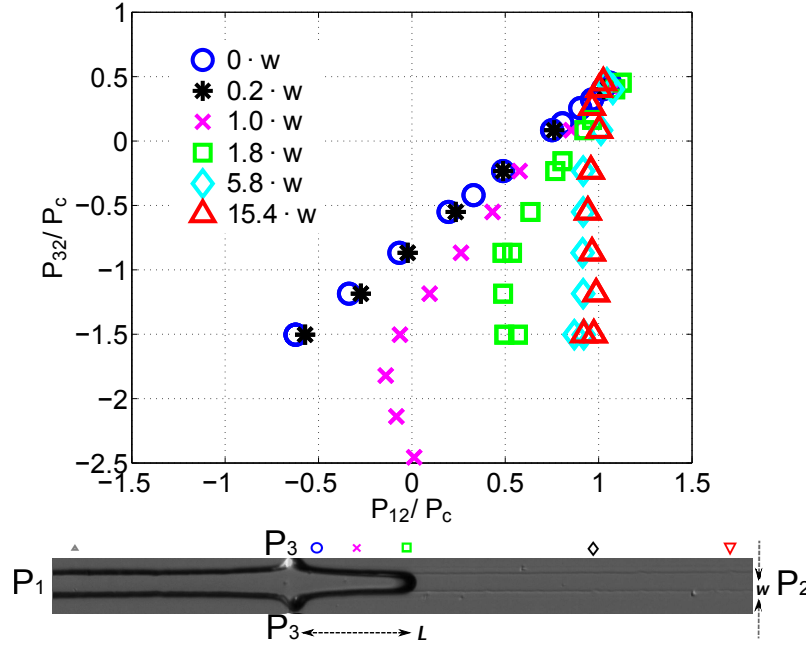


Figure 5.10: Diagram of couples of pressure drops to stabilize the meniscus at different positions. Each series of pressures corresponds to a position marked with a type of symbol.

5.4 Hydrodynamic resistance model

5.4.1 Hydrodynamic resistance

In the following, we will model the previous result by invoking hydrodynamic coupling between the two liquids.

Before deeming into the model, we recall some notions dealing with hydrodynamic resistance.

The pressure-driven, steady-state flow of a liquid through long, straight and rigid channels of any constant cross sectional shape is referred to as Hagen-Poiseuille (or simply Poiseuille) flow, and it is often characterized by the hydraulic resistance, $R_{hyd} = \Delta P/Q$, where ΔP is the pressure drop along the channel and Q is the flow rate through the channel. There is an analogy with electrical circuits: pressure drop corresponds to potential difference and flow rate to current. This analogy is rigorous at very low Reynolds numbers [136].

An arbitrarily shaped cross-section Ω in the xy plane for a straight channel placed along the z axis. A natural unit for the hydrodynamic resistance is given by dimensional analysis as

$$R_{hyd} = \eta L / \mathcal{A}^2 \quad (5.2)$$

where L is the channel length, η the dynamic viscosity of the liquid, $\mathcal{A} = \int_{\Omega} dx dy$ the cross-sectional area.

In this work, we just consider the mean velocity in the microchannels. Flow rate could

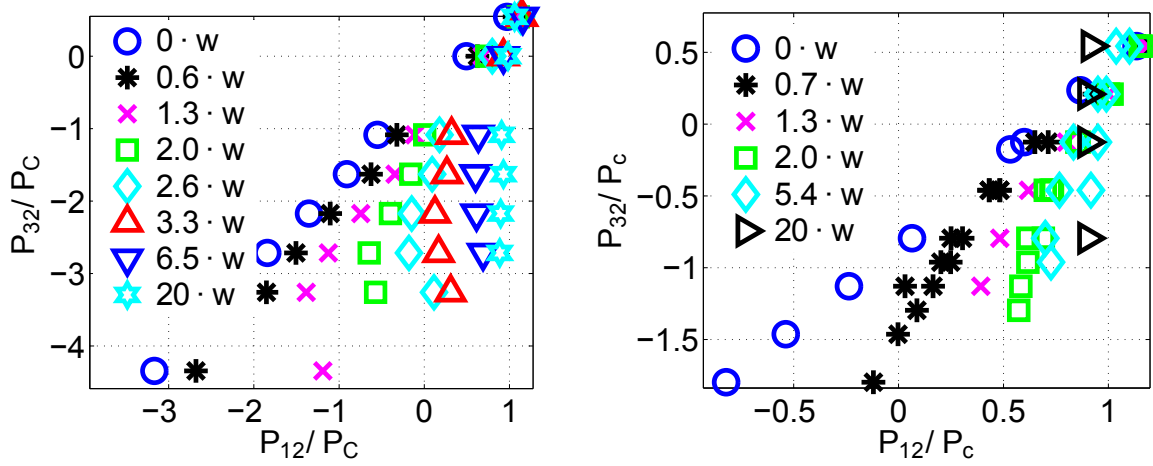


Figure 5.11: Two other complete wetting systems. Left: FC-72/silicone oil V5/PDMS, Right: FC-40/silicone oil V20/PDMS.

be reduced as $Q = v \cdot \mathcal{A}S$, where v is mean flow velocity and S is the sectional area. The hydrodynamic resistance becomes $R_{hyd} = \Delta P / (v \cdot \mathcal{A})$. Typically, we use $R_h \equiv R_{hyd} \mathcal{A} = \alpha \eta L / x^2$, where α is dimensionless geometrical correction factor, x is a length for various cross section shapes: circular, rectangular and triangular. α is characterized by its given shape [137], as shown in Table 5.2.

Here, we calculate the prefactor α of a circular sectional surface. We assume that the inertial forces are negligible in front of the viscous ones. Under such hypothesis, Navier-Stokes equations simplify to give the Stokes equations.

$$\eta \Delta v = \nabla P \quad (5.3)$$

where:

$$\eta \Delta v_z = \frac{\partial^2 v_z}{\partial z^2} + \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial v_z}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 v_z}{\partial \theta^2} \quad (5.4)$$

For a velocity v that does not depend upon z and θ , Equation 5.3 becomes:

$$\Delta v_z = \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial v_z}{\partial r} \right) \quad (5.5)$$

As P depends only upon z , we get:

$$\eta \frac{\partial v_z}{\partial r} = \partial_z P \frac{r}{2} \quad (5.6)$$

where, η is the viscosity of liquid, v_z is the velocity along the channel, $\partial_z P$ is pressure drop along the channel.

Solving this equation under the boundary condition $v_z(r = r_i) = v(r_i)$ leads to:

$$v_z(0 \leq r \leq r_i) = \frac{\partial_z P}{\eta} \left(\frac{r^2}{4} - \frac{r_i^2}{4} \right) + v(r_i) \quad (5.7)$$

The mean velocity through this channel is given by:

$$\bar{v}_z = \frac{\int v_z dS_i}{S_i} \quad (5.8)$$

S_i is the circle with radius $r = r_i$.

$$\bar{v}_z = -\partial_z P\left(\frac{S}{8\eta\pi}\right) + v(r_i) \quad (5.9)$$

If there is not slip at the wall, we get $v(r_i) = 0$. In this situation the prefactor is $\alpha = 8$.

Cross section shape		α
Circular	$x = R$	8
Rectangular ($h \leq w$)	$x = h = w$	28.4
	$x = h = 1/2w$	17.5
	$x = h = 1/10w$	12.8
Triangular (a, b, c)	$x = a = b = c$	34.6
	$x = a = b = \sqrt{2}/2c$	38.4

Table 5.2: $R_h = \alpha\eta L/x^2$ for channels with various cross section shapes: circular with radius R , rectangular with width w , height h and triangular with sides of lengths a, b, c .

Similar to Kirchhoff's junction and loop rules in electrical circuits, the hydrodynamics resistances also obey these laws. For a junction in a channels' network, the algebraic sum of flow rates is zero. We have equivalently the loop rule for a closed channels loop. As a result, the hydrodynamic circuits could be treated as electrical resistor networks (pressure drop is equivalent to the electric potential, flow rate is equivalent to the current, and hydrodynamic resistance plays the same role as the Ohm's resistance). Further, the hydrodynamic resistances obey similar rules in series or parallel circuits: Two resistances R_{h1} and R_{h2} in series and in parallel are equivalent to a resistance shown in Equation 5.11.

$$\textbf{Series:} \quad R_h = R_{h1} + R_{h2} \quad (5.10)$$

$$\textbf{Parallel:} \quad \frac{1}{R_h} = \frac{1}{R_{h1}} + \frac{1}{R_{h2}} \quad (5.11)$$

5.4.2 Hydrodynamic resistance model

At the corners of a rectangular-section channel under complete wetting, capillarity requires the wetting liquid along the corners. We note the pressures near the junction as P_1^* , P_2^* and P_3^* in different channels, as sketched in Figure 5.12.

In general, the displacement of a meniscus is controlled by the local pressure drop $P_1^* - P_2^*$ as shown in Figure 5.7.

When the meniscus does not move, the pressure drop $P_1^* - P_2^*$ equilibrates the capillary pressure.

$$P_1^* - P_2^* = \gamma\left(\frac{2}{w} + \frac{2}{h}\right) = P_{Ca} \quad (5.12)$$

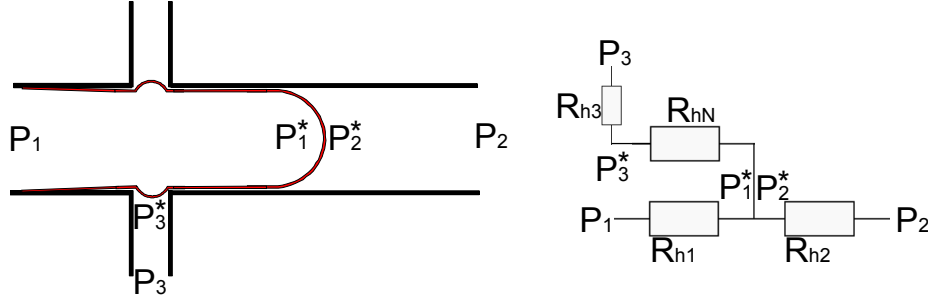


Figure 5.12: Left: local pressures as a result of pressure drops in the microchannels. Right: a hydrodynamic resistance schematic drawing for the biphasic flow at left.

As there is no flow in the main channel, the non wetting liquid has $v = 0$. As shown in Chapter 7 the mean velocity in the injected phase is equal to :

$$v = a^2 \left(-\frac{\partial_x P_1}{\eta_1} A_1(\epsilon, M) - \frac{\partial_x P_2}{\eta_2} B_1(\epsilon, M) \right) \quad (5.13)$$

As the meniscus does not move, we deduce a relation between the pressure drop in the injected fluid and the pressure drop in the wetting fluid.

$$\frac{\partial_x P_1}{\eta_1} A_1(\epsilon, M) = -\frac{\partial_x P_2}{\eta_2} B_1(\epsilon, M) \quad (5.14)$$

$$\partial_x P_1 = -\frac{\partial_x P_2 B_1(\epsilon, M) \eta_1}{\eta_2 A_1(\epsilon, M)} \quad (5.15)$$

Numerical estimate leads to B_1 less than 10^{-4} and A_1 around $1/28$. This clearly shows that the pressure drop in the nose is negligible in front of the pressure drop in the corners. In the following we will then assume that P_1 equals P_1^* and neglect $P_1^* - P_1$ in front of the others pressure drop. We thus write $P_1 = P_1^*$.

Wetting liquid flows may pass continuously through the wetting liquid and can be divided to three zones: in crossed channel, in main channel and though the corners. With the mass conservation, flow rates keep the same in the three zones:

$$\frac{(P_2 - P_2^*) S_2}{R_{h2}} = \frac{(P_2^* - P_3^*) S_N}{R_{hN}} = \frac{(P_3^* - P_3) S_3}{R_{h3}} \quad (5.16)$$

where R_{hi} , ($i = 1, 2, 3$ or N), is hydrodynamic resistance. And with definition $R_{hN} = \alpha L \eta / r_c^2$, where α is a geometrical correction factor [137], r_c is the width of corner flow. In the following, we will estimate α using the results from 7.

Near the crossed channel of the junction, the biphasic interface is in equilibrium by capillarity:

$$\frac{\gamma}{r_c} = P_1^* - P_3^* \quad (5.17)$$

Substituting P_1^* , P_2^* and P_3^* with above expressions, we get:

$$\frac{P_{32}R_{h2}}{(P_{12} - P_{Ca})S_2} - \left(\frac{R_{h2}}{S_2} + \frac{R_{h3}}{S_3}\right) = \frac{\alpha L \eta}{(4 - \pi)\gamma^4} (P_{12} - P_{32} + (P_{12} - P_{Ca})\frac{R_{h3}S_2}{R_{h2}S_3})^4 \quad (5.18)$$

Using dimensionless variable we get:

$$\frac{\tilde{P}_{32}}{\tilde{P}_{12} - 1} - \left(1 + \frac{R_{h3}S_2}{R_{h2}S_3}\right) = \frac{4^4 \alpha L}{(4 - \pi)L_c \alpha'} (\tilde{P}_{12} - \tilde{P}_{32} + (\tilde{P}_{12} - 1)\frac{R_{h3}S_2}{R_{h2}S_3})^4 \quad (5.19)$$

Equation 5.19 shows the relationship between the pressure drops $\tilde{P}_{12}$, $\tilde{P}_{32}$ and nose length L to stabilize the liquid-liquid meniscus near the junction. With a MATLAB program, we calculate a couple of pressure drops for each L , which stabilize the meniscus. With several length L , a diagram could be traced, which displays the stationary states of a meniscus in Figure 5.10.

The model predicts qualitatively the experiments. In the following section, we look for a quantitative comparison.

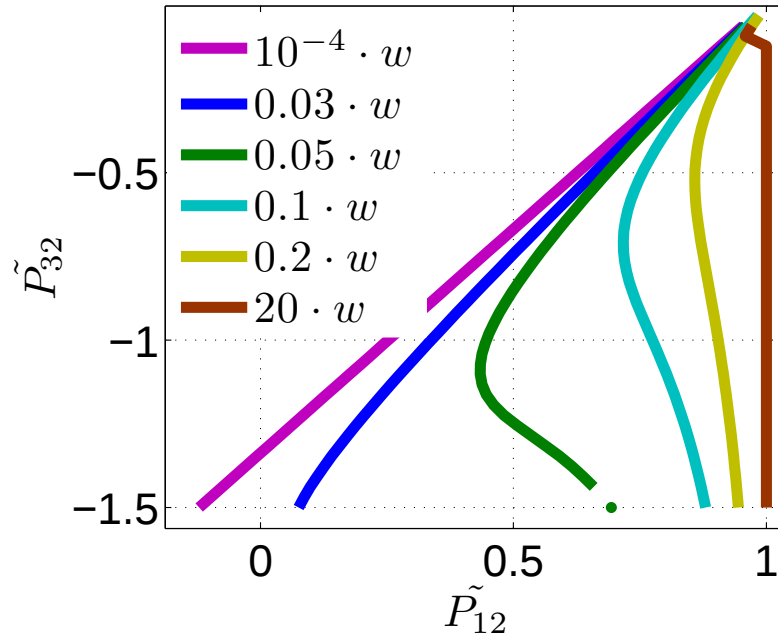


Figure 5.13: Modelling diagram of couples of pressure drops to stabilize the meniscus at different positions. Each series of pressures corresponds to a position marked with a color.

5.4.3 Comparison between the model and the experimental data

Let us first discuss, two limit behaviors. When the meniscus is before the junction, there are no corners and L is equal to zero. The meniscus in equilibrium gives a simplified

equation of Equation 5.18:

$$\tilde{P}_{32} = (\tilde{P}_{12} - 1)(1 + \frac{R_{h3}S_2}{R_{h2}S_3}) = A(\tilde{P}_{12} - 1) \quad (5.20)$$

This leads to a linear relation between $\tilde{P}_{12}$ et $\tilde{P}_{32}$ with a slope of $A=1.43$ in our geometry. This slope agrees well with the measured slope in Figure 5.8. Experimentally, we found $A = 1.19, 1.16$ and 1.18 in the various systems: FC-40/dodecane, FC-40/silicone oil V5, FC-72/silicone oil V20, respectively.

When the meniscus is far from the junction, the R_h in corner becomes big. Equation 5.16 is simplified to $P_2^* = P_2$, $P_3^* = P_3$ and $\tilde{P}_{12} = 1$.

The displacement of the meniscus does not depend upon P_{32} as sketched in Figure 5.9. At this stage, we note a first disagreement. $\tilde{P}_{32}$ does not vanish for $\tilde{P}_{12} = 1$. This is due to the deformation of the PDMS near the junction. The size of the channel varies in this region. This induces a change of the curvature of the meniscus at rest, and thus a variation of the local value of P_{Ca} . In other word P_{Ca} depends upon the position in the channel. As we have not taken into account this variation in our model we get a non zero value of $\tilde{P}_{32}$ for $\tilde{P}_{12} = 1$. We recall that $\tilde{P}_{12}$ is calculated on a given capillary pressure which is a constant.

When L is not too large, R_{hN} in the corners is comparable with R_{h2} and R_{h3} , the equilibrium states are described by Equation 5.18.

Figure 5.13 shows that the value of $\tilde{P}_{12}$ required to get a zero velocity depends upon $\tilde{P}_{32}$. The model describes qualitatively our data.

At this stage quantitative comparisons between our experiments and the model remain-difficult.

To fit our data, we miss the value of α . In our situation, the Chapter 7 predicts a value of α equal to 1000, by using the lubrication approximation theory.

To fit our data at least for L less than $3 \cdot w$, where w is the size of the channel, we use a value of α equal to 50. We believe that this disagreement is related to the shape of the meniscus. In chapter 7, we have assumed that the shape of the corner films does not depend on x , where x is the direction of the channel. When L is short, this rough estimate is not valid anymore.

These two points prevent us to give a quantitative comparison between our model and the data. However, we note that the value of required α to fit the data is in agreement with the modification of the corner shapes. Near the nose the corner films are thicker. This leads to a lower value for α .

5.4.4 Conclusion

We have studied the flow of a meniscus in a cross junction. We have developed a set up allowing us to control the pressure drop on both fluids. We show that the flow in the corner films modifies the value of the pressure drop required to stop the meniscus. In other words, the Laplace law seems to be no more valid. We have proposed a model that captures this

process. The use of the lubrication approximation avoids us to compare quantitatively our data and the model.

As an outlook, we propose to address this question in the partial wetting situation.

5.5 Summary

Corner flow around a meniscus

- Wetting fluid could exist in a wedge of a channel of irregular section. It can flow along the ducts and influences the displacement of meniscus. Its velocity depends on fluid properties (interfacial tension, viscosity), contact angle and geometry of the corner.
- Several complete wetting systems in a PDMS chip are used to study the meniscus dynamics.
- The meniscus in the main channel is controlled under two pressure drops. One of them is applied between the two liquids in main channel and another one through the corner wetting liquid. There is a strong coupling between the corner flows and the displacement of meniscus, when it lies in the vicinity of the junction (up to 10 times the channel width).
- Reverse flows in this PDMS chip are evidenced using confocal microscopy.

Flow diagram near a cross junction.

- We limit our study to an intermediate range of pressure. The drop of pressure $P_1 - P_3$ and $P_3 - P_2$ are low enough respectively to avoid the invasion of the cross channel and to induce drop formation at the junction.
- The coupling between the two pressure drops stabilizes the meniscus at different positions from the junction. A given position corresponds to a series of pressure drops.
- A flow diagram displaying the static position of the meniscus in the parameter plane drop of pressure in the internal fluid and drop of pressure in the external is displayed. Strikingly, it shows that the drop of pressure between the inlet and the outlet of the main channel required to stop the meniscus differs from the Laplace pressure. We note that it depends upon the drop of pressure applied on the inlet of the crossed channel.

Hydrodynamic resistance model

- Hydrodynamic resistance describes the pressure drop along the flow. The stabilized meniscus is a consequence of local pressure equilibrium.
- A model based on a network of adaptive hydrodynamic resistances is constructed. A qualitative agreement is found.

Chapter 6

Flows in corner films: theoretical approach

6.1 Introduction

During the invasion of a porous media by a non-wetting fluid, the pore size heterogeneity induces capillary fingering that leads to the formation of preferential path in the medium. After the percolation, the structure does not significantly evolves, and a steady state flow in a partially saturated medium occurs. The corresponding residual saturation could be rather low if the invasion has been performed at low capillary numbers. The non-wetting phase is organized in ganglions and clusters that occupy principally the smallest pores, *i.e.* the locations where the capillary pressures is maximum. If the flow is continuous, a steady state is reached, which implies that these clusters are rather stable [80].

The possibility of mobilizing these trapped clusters is of particular interest for many application, including oil recovery. Classical methods rely on an increase of the capillary number after the invasion step. By doing so, it is possible to decrease significantly the residual oil saturation, but the required capillary numbers are usually higher than 10^{-3} or 10^{-2} . Such values are either hard to reach or either out of the possible range, if one puts aside the very special case of ultra-low interfacial tensions.

The mobilization mechanism that is known to occur is based on phase displacement driven by pressure differences due to viscous forces [138]. The mobilization of trapped cluster in zones of low permeability, it has been shown at least in idealized micromodels of porous media that a simple pressure balance could account for the critical capillary number above which the residual clusters are displaced. The viscous pressure drop along a given cluster has to overcome a fraction of the capillary pressure of the trapped phase [139]. This can lead to rather high critical capillary number, especially for small clusters or ganglions, since the viscous pressure drop is proportional to the cluster size. Pore scale simulations illustrated moreover that cluster mobilization is simultaneous with break up, leading to smaller cluster that are more and more difficult to displaced.

We propose here that another drainage mechanism could play a great role, provided

that the displaced wetting fluid has a small contact angle. Under these conditions, since the pores or the media are of arbitrary shapes, we expect the fluids to coexist inside one pore, due to capillarity. This effect is predominant in wedges of small opening angles.

The main idea of this drainage through the liquid wedges rely on finite volume argument for the displaced and on the fact that the main flow of the injected fluid entrain the wetting liquid by viscous forces. Therefore the liquid wedges are drained, and their size should decrease as time evolves. Since the size of these liquid wedge is closely related to the pressure difference between the two phases, this drainage of the wedge films lead to a pressure decrease in the cluster. Once this pressure is reduced below the capillary pressure of the small pores where the trapping has occurred, the cluster is no more in equilibrium and starts to empty itself through the corner films, avoiding the global displacement of the cluster. Contrary to the classical mechanism, we will demonstrate that there is no threshold, and that, though very slow, it also happens at very low capillary numbers.

This chapter presents a theoretical approach on corner films flows. Using the lubrication approximation we develop the equations governing the time and space change in the corner film size. These equations will be analyzed and solved, for the particular of a cluster drainage through the corner films.

6.2 General governing equations

6.2.1 Flows in corner films

Our aim here is to see how the flow inside the corner film or outside modifies its size, or alternatively how its presence modifies the flows.

For that purpose, we need to relate the velocity in both phases (inside and outside the corner film) to the pressure drops. In the low-Reynolds limit, this involves the resolution of Stokes equation, inside a rather complex geometry, that is schemed in Figure 6.1. It consists in a square tube, where there are corner films of radii ϵa . We assume that the tube is long and that the corner film size varies slowly, so that standard lubrication approximation could be used. In this framework, the velocity is oriented along the main axis of the channel, and the pressure in each phase only depends on x .

Stokes equation is then reduced to

$$\partial_x p_i = \frac{1}{a^2} \eta_i (\partial_y^2 + \partial_z^2) u_i \quad (6.1)$$

where u_i is the x component of the velocity in phase i ($i = 1, 2$), $\partial_x p_i$ is the pressure gradient in phase i and η_i its viscosity. The coordinate x and y are normalized by the size of the square a . The boundary conditions are no-slip on the solid surface, and, on the interface between the two phases, the velocity and the tangential stress continue, *i.e.* $u_1 = u_2$ and $\eta_1 \partial_n u_1 = \eta_2 \partial_n u_2$. Due to the linearity of the Stokes equation and of the boundary conditions, the mean velocities $v_i = \langle u_i \rangle$ are linear functions of the pressure

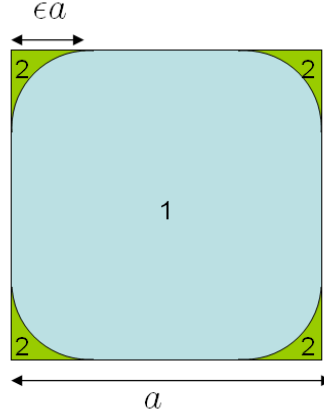


Figure 6.1: schematic drawing of the channel cross section that has corner films.

gradients and thus could be expressed by

$$\frac{v_i}{a^2} = -\frac{\partial_x p_1}{\eta_1} A_i(\epsilon, M) - \frac{\partial_x p_2}{\eta_2} B_i(\epsilon, M) \quad (6.2)$$

where we introduce the coefficients A_i and B_i that only depends on ϵ and $M = \eta_1/\eta_2$.

It is not easy to solve analytically this problem due to the complexity of the geometry and we use a numerical schematic drawing to obtain the coefficient A_i and B_i for various values of M and ϵ . The solution has been done with the software COMSOL by Bertrand Selva.

Figure 6.2 shows the variations A_i and B_i coefficients as function of M . A_1 and B_2 are in a first approximation independent on M , which is rather natural since M only changes the nature of the interface boundary condition. The others exhibits two asymptotic regimes, that are either a constant, either proportional to M , or inversely proportional to M .

	$M \ll 1$	$M \gg 1$	Empiric expression
A_1	$A_1^0(\epsilon)$	$A_1^\infty(\epsilon)$	$\frac{A_1^0 + A_1^\infty}{2} + \frac{A_1^0 - A_1^\infty}{2} \operatorname{erf}\left(\frac{1}{k} \log(M/M_0)\right)$
A_2	$A_2^\infty(\epsilon) M/M_0$	$A_2^\infty(\epsilon)$	$(A_2^\infty M/M_0) / \sqrt{1 + kM/M_0 + (M/M_0)^2}$
B_1	$B_1^0(\epsilon)$	$B_1^0(\epsilon) M_0/M$	$B_1^0 / \sqrt{1 + kM/M_0 + (M/M_0)^2}$
B_2	$B_2^0(\epsilon)$	$B_2^\infty(\epsilon)$	$\frac{B_2^0 + B_2^\infty}{2} + \frac{B_2^0 - B_2^\infty}{2} \operatorname{erf}\left(\frac{1}{k} \log(M/M_0)\right)$

Table 6.1: Empiric expressions of the coefficients A_i , B_i and their asymptotic behavior at low and high viscosity ratii.

Table 6.1 summarizes the asymptotics behavior of the coefficients as a function of M , and provides empiric expressions for intermediate values of M . As could be guessed from Figure 6.2, the constants k and M_0 appearing in the empiric expressions of Table 6.1 do not vary significantly when ϵ is varied, contrary to the asymptotic values. In fact, this approximation is strictly valid for low values of ϵ , but starts to fail when $\epsilon > 0.1$.

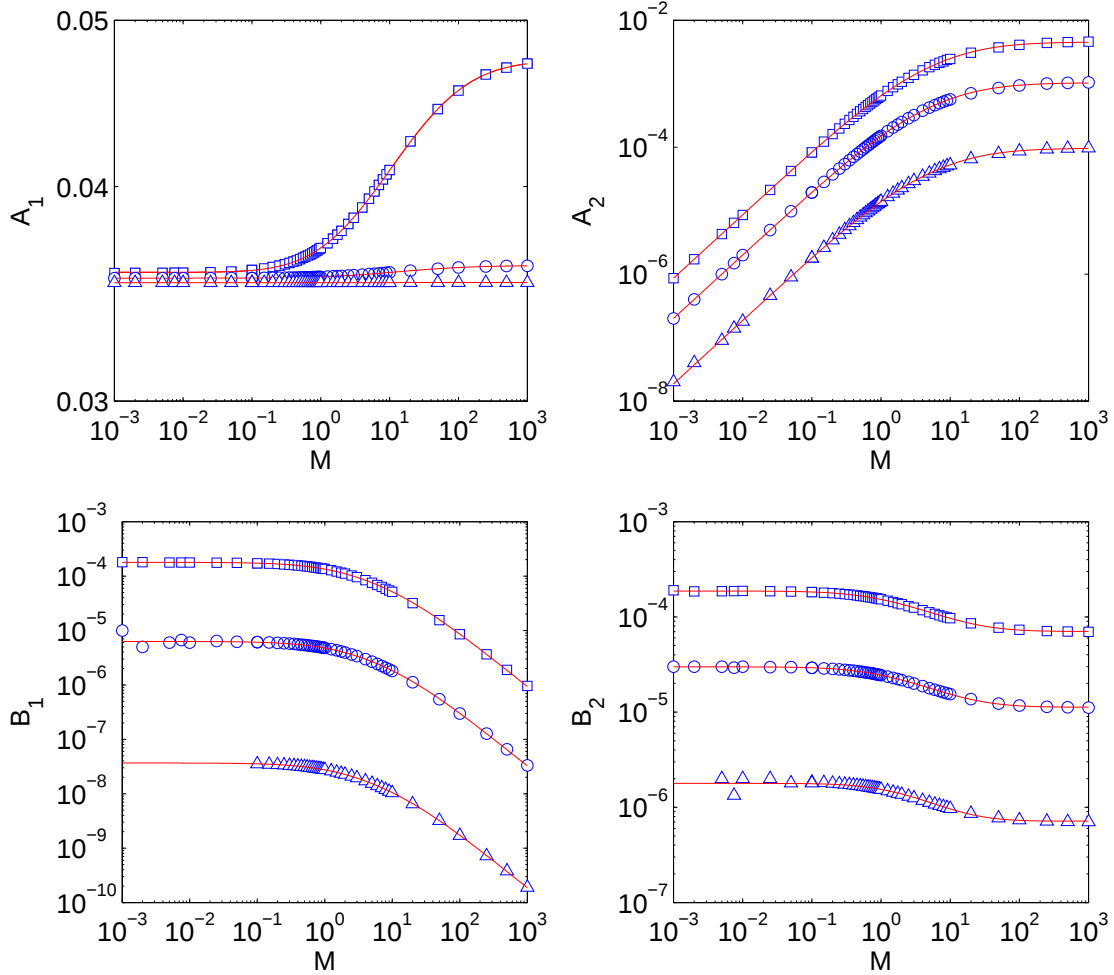


Figure 6.2: Calculated values of the coefficients A_1 , B_1 , A_2 and B_2 as a function of the viscosity ratio $M = \eta_1/\eta_2$, for three ϵ values : $\epsilon = 0.25$ (squares), $\epsilon = 0.1$ (circles), $\epsilon = 0.025$ (triangles).

6.2.2 Film size variations

In the previous section, we anticipate that the pressure gradient inside and outside the corner film could be different. However, the pressure difference between the two phases should verify Laplace law, which reads

$$p_1 - p_2 = \frac{\gamma}{a} \left(\frac{1}{\epsilon} + \frac{\partial_{x'}^2 \epsilon}{[1 + (\partial_{x'} \epsilon)^2]^{3/2}} \right) \quad (6.3)$$

where the second term of the right-hand side could be neglected, provided that we expect slowly varying films, where $x' = ax$. It is obvious from this equation that for uniform corner films, the two pressure drops are the same. It also implies that any film size variations lead to a difference in the pressure drops of the two phases.

Then the last step is to ensure volume conservation. This reads

$$\partial_t \epsilon^2 + \partial_x (\epsilon^2 v_2) = 0 \quad (6.4a)$$

$$\partial_x (\epsilon^2 v_2 + (1 - \epsilon^2) v_1) = 0 \quad (6.4b)$$

Equations 6.2, 6.3 and 6.4 form a complete system, for which the only approximation relies on the lubrication approximation, *i.e.* $\partial_x \epsilon \ll 1$.

6.3 Drainage of a trapped cluster through corner films

6.3.1 Stability conditions for a trapped cluster

In any complex geometries such as a porous media, the heterogeneity in pore sizes leads to phase trapping. We consider here that a wetting fluid is displaced by a non-wetting one at a fixed flow rate. At low capillary numbers, the flow is essentially governed by capillarity and the non-wetting fluid only invades the biggest pores, where the capillary pressure is minimum. This capillary fingering leads to phase trapping of the wetting fluid in the smallest pores, as depicted in Figure 6.3.

Once the cluster is formed, it could be displaced by a viscous pressure difference, which simply results from viscous forces. It is possible to show that these clusters of the non-wetting fluid are rather stable.

If one considers a single cluster of size ξ , its stability with respect to viscous forces is ensured by a capillary pressure difference between upstream and downstream menisci. This difference is coming from both the contact angle hysteresis (in partial wetting) and from meniscus accommodation with the geometry. One expects that the pressure difference is a fraction of the mean capillary pressure, given by γ/a (a being here the pore size). For the cluster to be stable, this pressure drop needs to dominate the viscous pressure drop, proportional to $\eta \xi V/a^2$. Thus there is a threshold in capillary number below which a cluster is stable even at long time, which is proportional to a/ξ . Such an analysis should be handled with care, since the capillary number used here is a "local" one, *i.e.* calculated from a local mean velocity. If the medium is only slightly saturated, this local velocity can be higher than the one estimated from the flow rate over the cross section area (Darcy velocity). Nevertheless, one sees that the threshold could be very high for small clusters, asking for a capillary number close to unity in order to be displaced. Importantly, below the threshold, the clusters are stable (for more details about the stability conditions, see References [80] and [139]).

In a porous medium, since the mechanism that leads to their formation is the same as the one used to mobilize them, we can directly conclude that all the clusters that are formed during the invasion of the medium at a fixed capillary number will remain stable unless the capillary number is increased by any means.

This mechanism of drainage thanks to viscous pressure drop is thus not present at low capillary numbers. We will now investigate in details the possibility of a drainage that could occur through the corner films. The mechanism is rather different since it is now

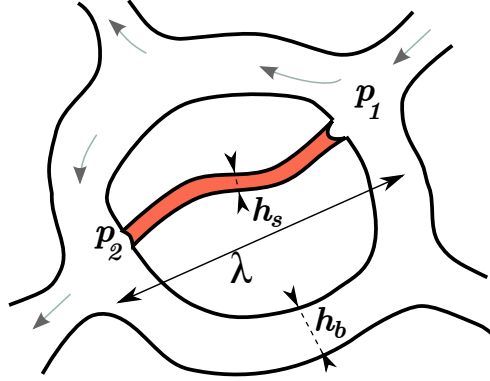


Figure 6.3: schematic drawing of a trapped cluster. Due to capillarity the wetting fluids (colored in the schematic drawing) is trapped in small pores.

the pressure difference between the two phases (and not the viscous pressure drop in the non-wetting phase) that increases.

6.3.2 Model geometry and assumptions.

Let us consider a straight channel of square cross section and of size a . Additionally, let us suppose that there exists a cluster located at $x = 0$, trapped by capillarity. The mean capillary pressure of this cluster is higher than that of straight channel.

Let us consider that the flow rate in phase 1 is imposed at a flow rate upon which the trapped cluster remains stable (in the sense of the viscous pressure drop mechanism), and, additionally that there exists a meniscus displacement inside the main channel. Close to that meniscus, the pressure difference between the two phases is $4\gamma/a$. Thus, just behind the meniscus where the second term of the right-hand side of Equation 6.3 is negligible, the size of the corner films is fixed at a value of $\epsilon_\infty = 1/4$.

According to the viscous entrainment by the flow in phase 1, we expect from Equation 6.2 that there exists a flow in phase 2. The main idea of the proposed mechanism relies on the fact that the flow rate of phase 2 is limited by finite volume (only phase 1 is injected). This should provoke a reduction of the corner film size, and thus a decrease of the pressure in phase 2. This reduction of p_2 should lead to the drainage of some cluster of the wetting phase trapped by capillarity. In order to describe this mechanism, we thus need to solve the size evolution of the corner films, together with the flow in these films.

6.3.3 Steady states in corner flows

Obviously from the set of equations, there exists a particular solution that is homogeneous, which is $\epsilon = \epsilon_\infty$. Switching from now on to non-dimensional quantities (the pressures being normalized by γ/a , the distance by a and the velocities by γ/η), and introducing the capillary number defined by $Ca = \eta_1 Q / a^2 \gamma$, where Q is the imposed flow rate. We obtain for the pressure gradients :

$$\partial_{x'} p'_1 = \partial_{x'} p'_2 = \frac{Ca}{(1 - c\epsilon_\infty^2)(A_1 + MB_1)} \quad (6.5)$$

where $c = (4 - \pi)/16$ is a constant, so that the total surface of the corner films reads $c\epsilon^2 a^2$. Thus there exists a flow in phase 2, the velocity $v'_2 = v_2 \eta_1 / \gamma$ being given by

$$v'_2{}^\infty = \frac{Ca(A_2 + MB_2)}{(1 - c\epsilon_\infty^2)(A_1 + MB_1)} \quad (6.6)$$

This mean velocity is of course lower than that of phase 1. If one notes as Γ the ratio of the mean velocities, it is given by

$$\Gamma = v_2^\infty / v_1^\infty = \frac{A_2 + MB_2}{A_1 + MB_1} \ll 1 \quad (6.7)$$

This particular solution thus could hold only if a continuous flow of the phase 2 is allowed. In the following, we suppose on the contrary that this flow is limited and should thus vanish far from the meniscus.

6.3.4 Unsteady states

6.3.4.1 Governing equations

Let us now remove the steady state assumption, and assume that since the x variation of ϵ should be small, the pressure difference in between the two phase is simply $1/\epsilon$. For a sake of simplicity, let us assume that v_1 is given in a fixed flow rate experiment by $Ca/(1 - c\epsilon^2)$. This assumption corresponds to neglect the time variation of the corner film size in the conservation equation of phase 1. It is justified by the fact that the surface occupied by the film size is very small. It greatly simplifies the problem. Under this approximation (which in practice is rather justified) the pressure gradient in phase 1 could be obtained directly from Equation 6.2 and reads

$$\partial_{x'} p'_1 = -\frac{1}{A_1 + MB_1} \left(\frac{Ca}{1 - c\epsilon^2} + \frac{MB_1}{\epsilon^2} \partial_{x'} \epsilon \right) \quad (6.8)$$

Then, using Equation 6.2 for phase 2 and volume conservation in phase 2, we obtain the following evolution equation for ϵ , without further approximations:

$$\partial_{t'} \epsilon^2 + \partial_{x'} \left\{ \Gamma \frac{Ca\epsilon^2}{1 - c\epsilon^2} + M(\Gamma B_1 - B_2) \partial_{x'} \epsilon \right\} = 0 \quad (6.9)$$

where $t' = t\gamma/\eta_1 a$. Writing $\tilde{t} = t' M Ca^2$, and $\tilde{x} = x Ca/a$, the equation do not depend on Ca and may be written in the more compact form:

$$\partial_{\tilde{t}} \epsilon^2 + \partial_{\tilde{x}} [f(\epsilon, M)\epsilon^2 - g(\epsilon, M) \partial_{\tilde{x}} \epsilon] = 0 \quad (6.10)$$

where

$$f = \frac{1}{M} \frac{\Gamma}{1 - c\epsilon^2} \quad (6.11a)$$

$$g = -\Gamma B_1 + B_2 \simeq B_2 \quad (6.11b)$$

Thus the characteristic time involved in the size change of corner films is $\eta_2 a / \gamma Ca^2$. The natural length scale for the distance is a / Ca . The lubrication approximation is thus appropriate for $Ca \ll 1$.

Figures 6.5 and 6.6 display the evolution of the function f and g as a function of M and ϵ , respectively. Concerning the ϵ dependance, f and g scale like ϵ^2 at the lower order in ϵ . They are fitted using a polynomial function of degree 4 in order to account for the deviations from this scaling for $\epsilon > 0.1$.

f and g reach asymptotic values for low and high M , that are given by :

$$f(M \rightarrow 0) = A_2^\infty / M_0 + B_2^0 \quad (6.12a)$$

$$f(M \rightarrow \infty) = B_2^\infty / (A_1^\infty + B_1^0 M_0) \quad (6.12b)$$

$$g(M \rightarrow 0) = B_2^0 \quad (6.12c)$$

$$g(M \rightarrow \infty) = B_2^\infty - B_1^0 B_2^\infty M_0 / (A_1^\infty + B_1^0 M_0) \quad (6.12d)$$

These functions are plotted in Figure 6.4.

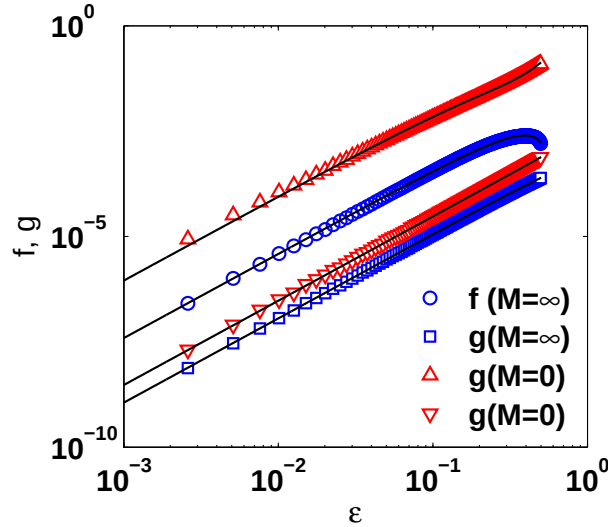


Figure 6.4:

For any values of M , $g < f$ by at least one order of magnitude. Both are increasing

function of ϵ . For arbitrary values of M and ϵ , f and g are fitted by:

$$f = \frac{f_\infty(\epsilon) + f_0(\epsilon)}{2} + \frac{f_\infty(\epsilon) - f_0(\epsilon)}{2} \operatorname{erf} \left(1.15 \log \frac{M}{M_f^0(\epsilon)} \right) \quad (6.13a)$$

$$g = \frac{g_\infty(\epsilon) + g_0(\epsilon)}{2} + \frac{g_\infty(\epsilon) - g_0(\epsilon)}{2} \operatorname{erf} \left(1.15 \log \frac{M}{M_g^0(\epsilon)} \right) \quad (6.13b)$$

where

$$f_\infty = 0.0399\epsilon^2 - 0.0508\epsilon^3 - 0.0386\epsilon^4 \quad (6.14a)$$

$$f_0 = 0.8891\epsilon^2 - 2.371\epsilon^3 + 2.841\epsilon^4 \quad (6.14b)$$

$$M_f^0 = 3.393 + 0.8408\epsilon - 11.50\epsilon^2 - 18.86\epsilon^3 + 43.64\epsilon^4 \quad (6.14c)$$

$$g_\infty = (1.1389\epsilon^2 - 0.1167\epsilon^3 - 0.3930\epsilon^4) \times 10^{-3} \quad (6.14d)$$

$$g_0 = (2.984\epsilon^2 + 0.1189\epsilon^3 - 0.0006\epsilon^4) \times 10^{-3} \quad (6.14e)$$

$$M_g^0 = 2.602 + 0.4747\epsilon - 5.5541\epsilon^2 - 12.77\epsilon^3 + 21.96\epsilon^4 \quad (6.14f)$$

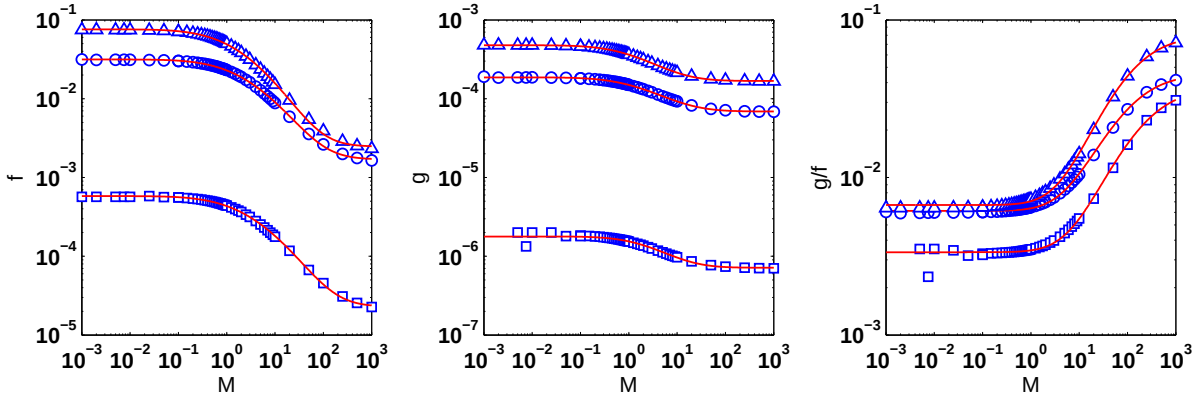


Figure 6.5: Calculated values of f and g as a function of the viscosity ratio $M = \eta_1/\eta_2$, for three values of ϵ : $\epsilon = 0.025$ (squares), $\epsilon = 0.1$ (circles), $\epsilon = 0.25$ (triangles).

It is interesting to note that the first non-vanishing coefficient of the Taylor expansion of f and g is the ϵ^2 term. Therefore, the governing Equation 6.10 could be approximated for $\epsilon \ll 1$ by:

$$\partial_t \epsilon^2 + \partial_{\bar{x}} [\alpha \epsilon^4 - \beta \epsilon^2 \partial_{\bar{x}} \epsilon] = 0 \quad (6.15)$$

where α and β depend on M .

6.3.4.2 Comments on the governing equations

We have already discussed that one general solution of the problem is to have a uniform corner flow thickness, leading to similar pressure gradients in both phases. We now envisage

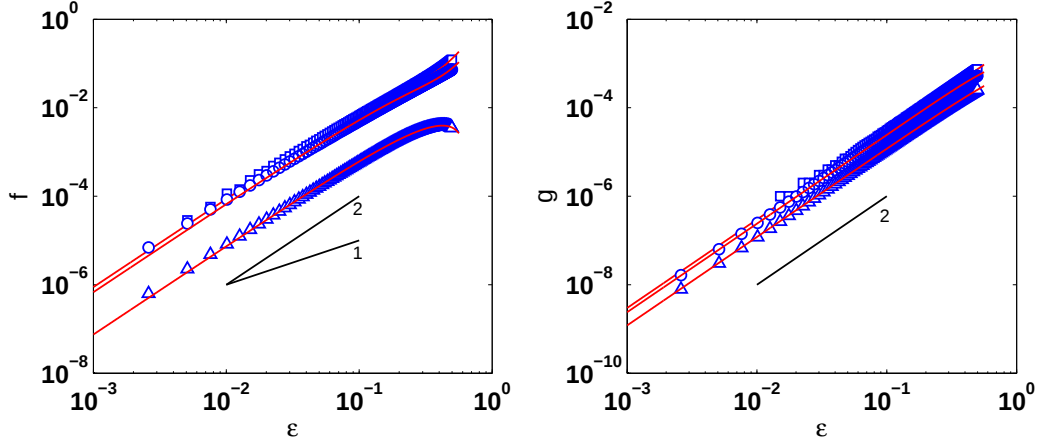


Figure 6.6: Calculated values of the functions f and g as a function of ϵ , for three values of M : $M = 10^{-2}$ (squares), $M = 1$ (circles), $M = 10^2$ (triangles).

some situations where this solution does not match the left boundary conditions. As already discussed, the film size near any moving meniscus is $\epsilon_\infty = 1/4$, corresponding to a velocity in phase 2 given by Equation 6.6.

Therefore, if one fixes at a given location either the flow rate in phase 2, or the film size (or equivalently the pressure difference between the two phases), the uniform solution is no more suitable near this location.

Let us have a look at the linearized equation around a $\epsilon = \epsilon_\infty$. Equation 6.10 is then given at the first order in $\xi = \epsilon - \epsilon_\infty$ by:

$$\partial_{\tilde{t}}\xi + u_\infty \partial_{\tilde{x}}\xi - \frac{g(\epsilon = \epsilon_\infty)}{2\epsilon_\infty} \partial_{\tilde{x}}^2 \xi = 0 \quad (6.16)$$

where

$$u_\infty = \frac{1}{2\epsilon_\infty} \left. \frac{\partial f \epsilon^2}{\partial \epsilon} \right|_{\epsilon = \epsilon_\infty} \quad (6.17)$$

It corresponds to a standard 1-dimensional transport equation with a velocity u_∞ . It could be easily verified that this velocity is much lower than the meniscus velocity, $d\tilde{x}_m/d\tilde{t} \simeq 1$. Indeed, it is always below typically a few percent. We find $u_\infty = 0.052$ for $M \rightarrow 0$ and $u_\infty = 2.6 \times 10^{-3}$ for $M \rightarrow \infty$. The meniscus velocity is $\dot{x}_m = Q_1/a^2 (1 - c\epsilon_\infty^2)$, which reads in the adimensional form $d\tilde{x}_m/d\tilde{t} = 1/(1 - c\epsilon_\infty^2) \simeq 1$. The third terms (the equivalent diffusion term) has a rather low coefficient (a few 10^{-3}).

The fact that $u_\infty \ll \dot{x}_m$ has some important consequences since it implies that any variations of the film size will be convected slower than the meniscus. It also implies that the asymptotic solution near the meniscus is a uniform film thickness, $\epsilon(x) = \epsilon_\infty$. It is thus possible to state that translating the right boundary conditions towards infinity will not change the solution. From a numerical point of view, this boundary condition could be fixed at a given arbitrary location, far enough from $x = 0$.

6.3.5 Solutions with no flow rate in the corner films

6.3.5.1 Numerical solution

We solve Equation 6.10 with a left boundary conditions that is no flow rate at $x = 0$, i.e. $\epsilon^2 f - g \partial_{\tilde{x}} \epsilon = 0$. This boundary condition represents the case of a trapped cluster at $x = 0$. The right boundary condition is obtained close to the meniscus, where $\epsilon = \epsilon_\infty = 1/4$. The meniscus velocity is given at any time by the mean value in phase 1, in the meniscus region. Thus, at fixed flow rate in phase 1, the meniscus velocity is given by $v_1 = (\gamma/\eta_1) Cat / (1 - \epsilon_\infty^2)$ (in physical units).

We first solve numerically the equation. Figure 6.7 displays a typical results. One can easily verify that for $\tilde{x} > u_\infty \tilde{t}$, the film size is unperturbed and equals the right boundary condition value. It decreases near $x = 0$ due to the no flow condition.

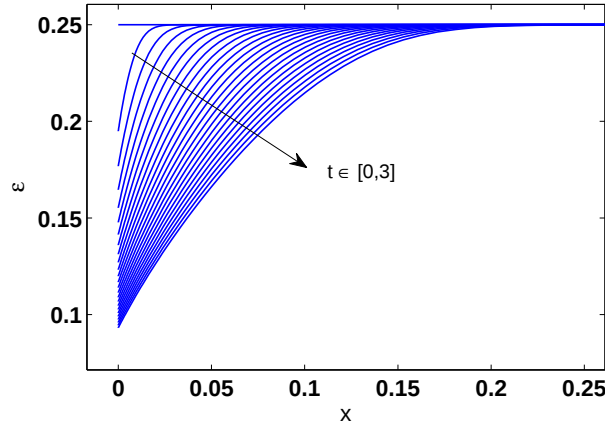


Figure 6.7: Solutions obtained for $M = 1$.

Figure 6.8 focus on the evolution of the film size at $x = 0$. This evolution depends on M but exhibits two distinct regimes. At very short time (i.e. when $\epsilon(0, t) \simeq \epsilon_\infty$), $\Delta\epsilon \sim t^{-1/2}$. At long time (i.e. when $\epsilon \ll \epsilon_\infty$), $\epsilon \sim t^{-1/3}$. These two asymptotic regimes will be discussed in the following sections.

The delay t_c necessary to reach a given value ϵ_c at $x = 0$ only depends on M . An example is shown in Figure 6.9. Similarly to the function f/g , there are asymptotic values for low and high M . Note that the transition between the two asymptotic values occurs at M greater than 1. In the transition region, $\tilde{t}_c \propto M$.

6.3.5.2 Asymptotic solution for long time

Let us try to find an asymptotic solution at long time. We start from Equation 6.15 that is valid for low values of ϵ . It might be rewritten in the following form:

$$\partial_{\tilde{t}} \epsilon + 2\alpha \epsilon^2 \partial_{\tilde{x}} \epsilon - \beta (\partial_{\tilde{x}} \epsilon)^2 - \frac{\beta}{2} \epsilon \partial_{\tilde{x}}^2 \epsilon = 0 \quad (6.18)$$

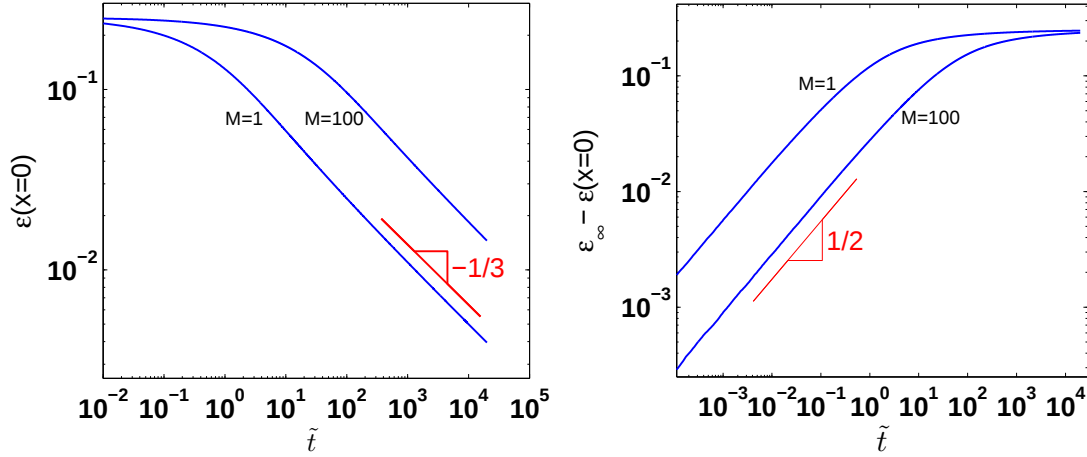


Figure 6.8: Evolution of the film size at $x = 0$ for two viscosity ratios M . Note that these two values are nearly the two extreme limits since f/g only varies in the interval 1-100.

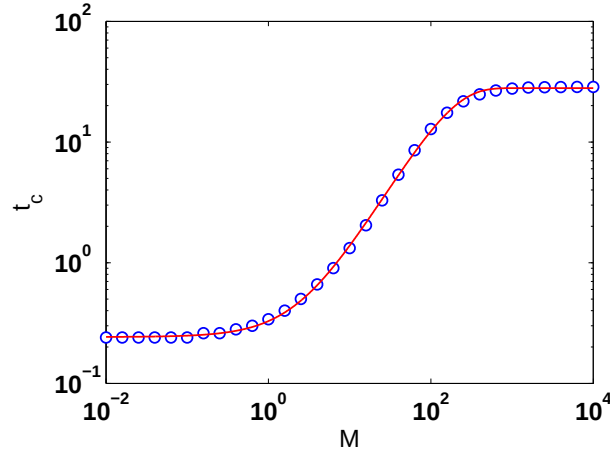


Figure 6.9: Delay time t_c at which the corner film size at $x = 0$ reaches the value $\epsilon_0 = 1/6$. The solid line represents the best fit obtained using the following empiric function: $t_c(M) = t_c^\infty - (t_c^\infty - t_c^0) \exp \left[- (M/M_c)^k \right]$, with $t_c^\infty = 28$, $t_c^0 = 0.24$, $M_c = 165$ and $k = 1.13$.

Let us rescale again time, space and ϵ , so that this equation reduces to:

$$\partial_{\tilde{t}} e + e^2 \partial_{\tilde{x}} e - \frac{1}{2} (\partial_{\tilde{x}} e)^2 - \frac{1}{4} e \partial_{\tilde{x}}^2 e = 0 \quad (6.19)$$

where $e = \epsilon/\epsilon_\infty$, $\tilde{t} = \alpha^2 \epsilon_\infty^3 \tilde{t}/\beta$ and $\tilde{x} = \alpha \epsilon_\infty \tilde{x}/\beta$. The boundary conditions are $e(\infty, \tilde{t}) = 1$ and $\partial_{\tilde{x}} e|_{\tilde{x}=0} = e(0, \tilde{t})^2$.

We then assume that the two first terms of Equation 6.19 are dominant, except for small and big x . The resulting approximate equation reads $\partial_{\tilde{t}} e + e^2 \partial_{\tilde{x}} e = 0$, for which the

general solution e is solution of

$$\phi(e)e^2 + te^2 - x = 0 \quad (6.20)$$

This solution could not match the right boundary conditions, $e = 1$ for $x \rightarrow \infty$. However, as already discussed, we expect that a constant solution is obtain for $\bar{x} > \bar{t}$. We thus transform the right boundary conditions into $e(\bar{x} = \bar{t}, \bar{t}) = 1$, and solve the equation for $\bar{x} < \bar{t}$. This implies that $\phi(1) = 0$. Then, we simply match the solution for $x \rightarrow 0$. On the other hand, the left boundary conditions allow to express e as $e = e_0 + xe_0^2 + \mathcal{O}(x^2)$, where $e_0 = e(0, t)$. Inserting this developpement in Equation 6.20, we obtain:

$$e_0^2(\phi(e_0) + t) - x [e_0^4\phi'(e_0) + e_0^3\phi(e_0) + te_0^3 - 1] + \mathcal{O}(x^2) = 0 \quad (6.21)$$

Straightforward identification then leads to

$$\begin{cases} e_0^4\phi'(e_0) - 1 = 0 \\ \phi(e_0) = -t \end{cases} \quad (6.22)$$

Finally, using the fact that $\phi(1) = 0$, the function ϕ is given by $\phi = (1 - 1/e^3)/3$. We can thus deduce directly the time evolution of e_0 , i.e. $e_0 = (3t + 1)^{-1/3}$. Note that this is very good agreement with the scaling found for the numerical solution (see Section 6.3.5.1 and Figure 6.8). The complete solution for e could be obtained from Equation 6.20, and is solution of

$$e^3(3t + 1) - 3xe - 1 = 0, \quad (6.23)$$

for which the single real root is expressed as

$$e(x, t) = 2^{1/3} \frac{2^{-2/3} (1 + 3t)^{4/3} \left(1 + \sqrt{1 - \frac{4x^3}{1+3t}}\right)^{2/3} + x + 3xt}{(1 + 3t)^{5/3} \left(1 + \sqrt{1 - \frac{4x^3}{1+3t}}\right)^{1/3}} \quad (6.24)$$

This solution constitutes a very good approximation at long time, since the space variations of e are small and thus the second order derivatives of e could be safely neglected, expect near $x = 0$. Figure 6.10 displays some comparisons between this asymptotic solutions and the numerical solution of Equation 6.19. The agreement is rather good at long time and for not too small x . It fails however at short time and for small x since the leading terms of Equation 6.19 are not the two first ones. For $x \ll 1$ even at long time the two last terms of the equation should become the leading ones since the size variation near $x = 0$ are rather big. It should thus be possible to obtain a better solution for small x by considering a matching to a solution at small x . This is left for future work.

6.3.5.3 Asymptotic solution for short time

At short time, one can obtain an asymptotic solution after linearizing Equation 6.19. The linearized equation reads:

$$\partial_t e + \partial_{\bar{x}} e - \frac{1}{4} \partial_{\bar{x}}^2 e = 0 \quad (6.25)$$

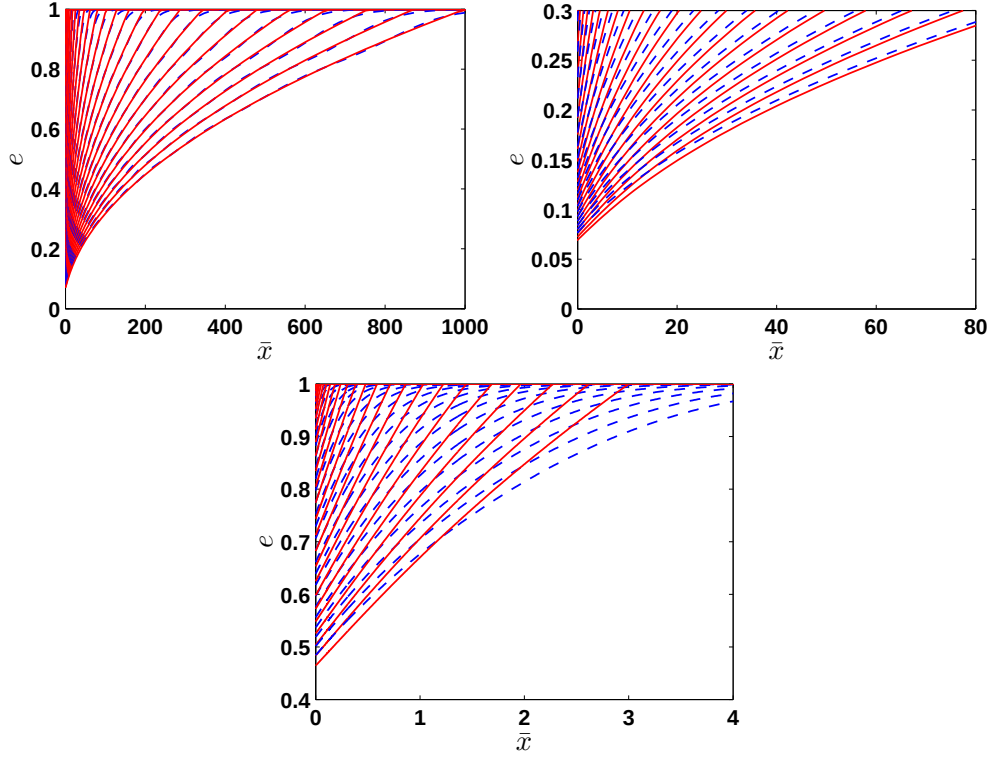


Figure 6.10: Blue dashed line : simulation. Red solid line : asymptotic solution (Equation 6.24). Top, solutions for $\bar{t} < 1000$ (right: zoom at small x). Bottom: short time comparison ($\bar{t} < 3$).

The solution of this equation, for a linearized left boundary condition that is $\partial_{\bar{x}}e = 1$, is straightforward since it corresponds to the classical solution of the heat equation at constant flux. The solution reads:

$$e = 1 + \bar{x} \operatorname{erfc} \left(\frac{\bar{x}}{\sqrt{\bar{t}}} \right) - \sqrt{\frac{\bar{t}}{\pi}} \exp \left(-\frac{\bar{x}^2}{\bar{t}} \right) \quad (6.26)$$

Figure 6.11 to a comparison between the solutions of the linearized equation. It is made in Figure 6.11 for $t < 10^{-2}$. One may notice that the solution of linearized equation starts to deviate significantly from the true solution for $t > 10^{-2}$.

Of particular interest is the variation of the film size at $x = 0$. It is given by:

$$e(0, t) = 1 - \sqrt{\frac{t}{\pi}} \quad (6.27)$$

6.3.6 Unsteady states with fixed values of ϵ at $x = 0$

Let us now envisage that at time t_c , the size of the corner film has reached the critical value for which the cluster is no more stable. The cluster will then start to empty inside

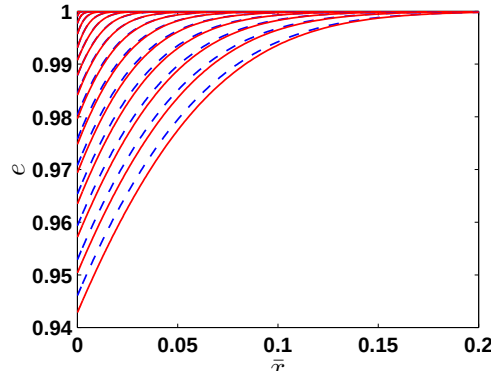


Figure 6.11: Comparison at short time ($t < 10^{-2}$) between the solution of Equation 6.19 and the one of the corresponding linearized equation.

the corner film. But because this involves movements of menisci, the pressure difference and consequently the size of the corner film is now fixed. Equation 6.10 thus need to be solved with a left boundary condition that is equal ϵ_0 .

The initial condition should be the profile obtained at the end of the first phase, where the film size is decreasing close to the cluster.

Figure 6.12 shows examples of the numerical resolution of equation 6.10. Similarly to the previous case, the corner film size is unperturbed at long distances x . Close to $x = 0$, a steady solution with $\epsilon = \epsilon_0$ is developping. The transition between these two flat region is simply convected and dispersed, with a velocity given by

$$u_0 = \frac{1}{2\epsilon_0} \frac{\partial f \epsilon^2}{\partial \epsilon} \bigg|_{\epsilon=\epsilon_0} \quad (6.28)$$

For $\tilde{x} < u_0 \tilde{t}$, the film size is approximately equal to ϵ_0 , meaning that the total flow in phase 2 at $x = 0$ is simply given by $f(\epsilon_0, M) c \epsilon^2$, and the mean velocity in phase 2 by $f(\epsilon_0, M)$.

Similarly to the previous section, it is possible to find an asymptotic solutions, provided that the leading terms should be the same as previously, in the transition region, *i.e.* for $x \in [v_0 t, v_\infty t]$.

6.3.7 Summary and discussion

6.3.7.1 Summary in physical units

Let us try to summarize the results obtained. We consider a cluster trapped in a region having a capillary pressure that is a fraction r of the main capillary pressure. The menisci ahead from this cluster advancing at a capillary number Ca will drain the corner films. The size of the corner films is at the beginning high enough to prevent the cluster to be drained. During this regime, the corner film is drained, and its size is decreased close to the cluster.

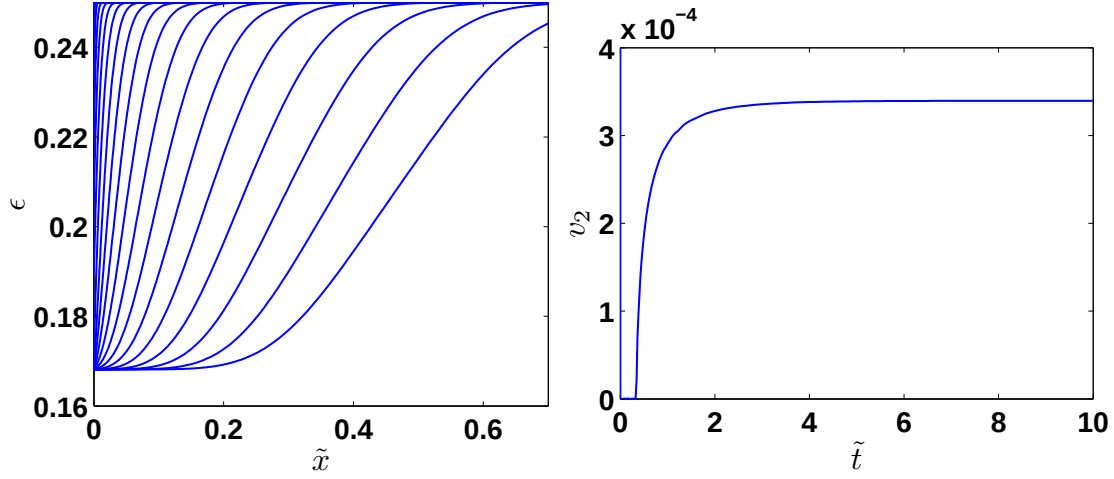


Figure 6.12: Left: numerical profiles of the corner films with fixed left boundary conditions $\epsilon_0 = 1/6$ in the case of $M = 1$. The different lines correspond to several time values ($\tilde{t} < 20$).

In a second regime, the corner film size has reached the size $r\epsilon_\infty a$ for which the cluster is no more stable: the pressure difference between the two phases is greater than the capillary pressure inside the trapped cluster. It is now the cluster that is drained, through the films. The main question is to know the rate at which this drainage occurs.

1st regime: film drainage The first regime, *film drainage*, exhibits the the following features:

- (i) The corner film size is unperturbed on a wide region near the advancing menisci, and remains equal to $\epsilon_\infty = 1/4$.
- (ii) Close to the cluster ($x = 0$), there is domain where the corner film size is decreasing. The characteristic length d of this domain is given at long time by

$$d = \frac{Q_1}{a^2} \frac{1}{2\epsilon_\infty} \partial_\epsilon (f\epsilon^2) \big|_{\epsilon=\epsilon_\infty} t \quad (6.29)$$

or in terms of Q_2 , simply by

$$d = \frac{1}{2c\epsilon_\infty a^2} \partial_\epsilon Q_2 \big|_{\epsilon=\epsilon_\infty} t \quad (6.30)$$

This drained region thus increases linearly with time, with a velocity in the order of the mean velocity in phase 2. For the usual case of $\epsilon = 1/4$, the above computations leads to

$$d \simeq 5.15 \times 10^{-2} \frac{Q_1}{a^2} t, \quad \text{for } M \ll 1 \quad (6.31a)$$

$$d \simeq 2.55 \times 10^{-3} \frac{Q_1}{a^2} t, \quad \text{for } M \gg 100 \quad (6.31b)$$

These asymptotic values of d are valid when $d > (g/f\epsilon_\infty)a/Ca \approx 10^{-1}a/Ca$, since at shorter time, the capillarity could not be neglected as compared to the convection and tends to enhance d . In the very short time limit, d should increase as

$$d \simeq a \sqrt{\frac{gM\gamma t}{2\epsilon_\infty}} \eta_1 a \approx 0.1 \sqrt{\frac{\gamma t}{\eta_2 a}} \quad (6.32)$$

However in this limit the value of $\epsilon(x=0)$ has not been significantly reduced.

- (iii) The corner size close to the trapped cluster decreases as a function of time. Again, we should distinguish between a short time region and a long time region. However, whatever the time scale, the time t_c necessary to reach a critical value of ϵ_c is proportional to the characteristic time of the problem and is thus given by:

$$t_c = \psi(\epsilon_c, M) \frac{a\eta_2}{\gamma Ca^2} \quad (6.33)$$

Though the function ψ depends on M , its variation is limited to the range $1 < M < 100$ where it increases (in fact in this range, $\psi \propto M$ and thus t_c only depends on η_1), since it reaches asymptotic values for low and high M . For example, for $\epsilon_c = 1/6$, the asymptotic values of ψ are 0.24 ($M \ll 1$) and 28 ($M \gg 100$).

At short time and long time, the asymptotic solutions allow to access the asymptotic behavior of the function ψ .

At short time, for $\epsilon(0, t) \simeq 1$, $\epsilon(0, t) = 1 - \sqrt{\alpha^2 \epsilon_\infty^3 \tilde{t} / \beta \pi}$, with $\tilde{t} = Ca^2 \gamma t / \eta_2 a$ and thus

$$\psi(\epsilon_c, M) = \frac{\beta \pi}{\alpha^2 \epsilon_\infty^3} (1 - \epsilon_c)^2 \quad (6.34)$$

At long time (and thus for $\epsilon(0, t) \ll \epsilon_\infty$), the asymptotic solutions allow to access the asymptotic behavior of the function ψ . Indeed, the film size decreases at long time as :

$$\epsilon(0, t) = \epsilon_\infty^2 (3\alpha^2 \tilde{t} / \beta)^{-1/3} \quad \text{with } \tilde{t} = Ca^2 \gamma t / \eta_2 a \quad (6.35)$$

Consequently,

$$\psi(\epsilon_c, M) = \frac{\beta}{3\alpha^2} \frac{\epsilon_\infty^{2/3}}{\epsilon_c^3} \approx \begin{cases} 0.02/\epsilon_c^3, & \text{for } M \ll 1 \\ 3.8/\epsilon_c^3, & \text{for } M \gg 100 \end{cases} \quad (6.36)$$

2nd regime: cluster drainage through corner films During this second regime, the cluster is emptying through the corner films for which the size close to the cluster is fixed by the capillary pressure in the trapped zone, i.e. $\epsilon = \epsilon_c = r\epsilon_\infty$. The main features of this regime are the following:

- (i) The film size basically exhibits three domains. For $x > d$, the corner film size is kept to $\epsilon_\infty = 1/4$. The distance d is still accounted by equation 6.29. For $x < d_c$, the corner film size equals the value close to the cluster. d_c is also given by Equation 6.29, provided that ϵ_∞ is replaced by ϵ_c . In between there is a transition region which width increases as a function of time and which is roughly linear.
- (ii) After a rather short transition, the flow rate is thus fixed in phase 2 and equals the flow rate of an homogeneous corner film of size ϵ_c :

$$Q_2 = c\epsilon_c^2 M f(\epsilon_c, M) Q_1 \quad (6.37)$$

Therefore, the flow rate in the displaced phase is always proportional to the main flow rate. For rather low values of ϵ , f is well approximated by $\alpha(M)\epsilon^2$. Thus Q_2 scales as ϵ^4 which greatly reduces the drainage rate if ϵ is small. Asymptotic values for extreme value of M are provided below :

$$\begin{cases} Q_2 \approx 5 \times 10^{-2} \epsilon_c^4 M Q_1, & \text{for } M \ll 1 \\ Q_2 \approx 2 \times 10^{-3} \epsilon_c^4 M Q_1, & \text{for } M \gg 100 \end{cases} \quad (6.38)$$

Therefore the drainage of the cluster is greatly enhanced for high values of M , but note that in the range 1-100, the flow rates is roughly independant on M .

6.3.7.2 Cluster at a fixed location $x_0 > 0$

It is tempting to enlarge the scope of the drainage mechanism presented here. During the drainage of a porous medium, if the wetting properties allow corner films, we expect from the previous analysis a drainage through the corner films. We recall that it is due to a finite volume of the wetting fluid. Thus this additional sweeping start from the inlet where the corner film size is progressively decreased. The porous medium contains in general many of these clusters located at various places.

Contrary to the previous analysis, they are not located at $x = 0$ (the inlet), as shown in the left part of Figure 6.13. It means that the delay time necessary to reach the critical value of ϵ_c could be much greater than the one calculated above. We envisage this case below. Using our analysis, it is rather straightforward (at least with the numerical solution), to determine the time needed to reach the corresponding critical value of the corner film size.

For a cluster located at a fixed position $\tilde{x}_0$, the scaling of the result is straightforward since the solution in non-dimensional units only depends on M . Thus we would expect a scaling for the delay time which is Ca^{-2} . However, this result is not really pertinent, since the characteristic length scale of the problem is $1/Ca$. Thus for a fixed physical length x_0 , the variations of the delay time when varying the capillary number are in general more complex since we need to use the time and space solution of the equation.

When $\tilde{x} \gg 1$ and for not too small values of ϵ , we can use the fact that the solution is simply convected at a velocity that is proportional to Ca . Thus the time (in physical unit) that is necessary to reach a given value ϵ_c at $x = x_0$ is proportional to x_0/Ca .

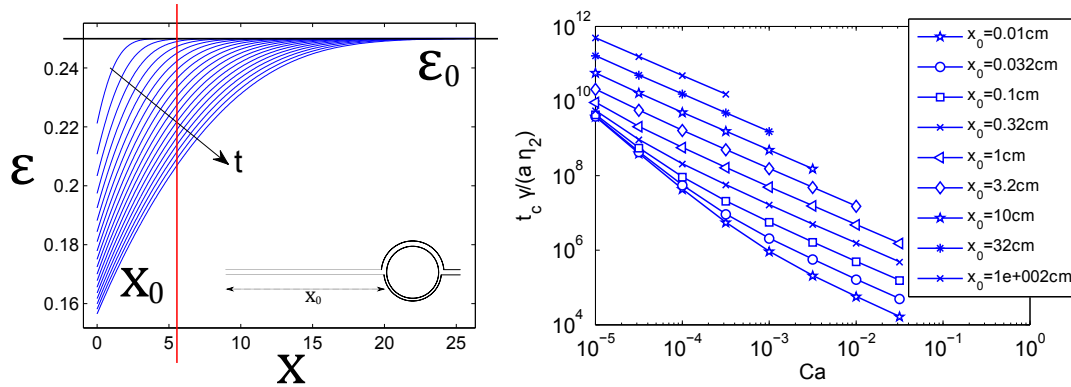


Figure 6.13: Left: The variation of time-resolved film size depends on the observation location x_0 . Right: Calculated values of the delay time t_c as a function of Ca , for $M = 1$ and for several cluster locations. The locations x_0 indicated in the legend stands for a channel of size $a = 50\mu\text{m}$. At low Ca and for small x , the data are proportional to Ca^{-2} . At high Ca or for larger x_0 , they scales like Ca^{-1} .

For $\tilde{x} \ll 1$, the solution is a bit more complex but since in this case the perturbation spreads independantly on the convection term, we can expect that a scaling in Ca^{-2} would hold in this regime, similarly to the $x = 0$ case.

Due to the complexity of the problem at fixed locations, we solve the problem numerically, as a function of Ca . The Figure 6.13 displays a piece of the results obtained. At high capillary numbers, $\tilde{x} \gg 1$ since $\tilde{x} = xCa/a$, and the delay time, at which the corner film size reaches the value ϵ_c , is proportional to $1/Ca$. The order of magnitude of the duration of the first regime where the corner film is drained depends greatly on the location. In the high- Ca regime, it increases linearly with the location x_0 . In the low Ca regime, it does not depends on x_0 .

From a pratical point of view, the numerical solutions allow to map the transition between the two regime. For $M = 1$, the transition is about $\tilde{x} \sim 10^{-3}$. It means that, unless the capillary number is very low, or if the cluster location is about the channel size, experiments always are in the high- Ca regime where the delay time scales proportionally to x_0/Ca .

A more detailed analysis might be interesting but ask for a significative amount of work. We limit ourselves in this part to draw a general picture and to run numerical solutions adapted to the experiments that are presented in the following chapter.

Once the corner film size has reached the value below the cluster is drained, the flow rate downstream is rapidly fixed by the steady value of the corner film. The analysis made for a cluster located at $x = 0$ thus holds directly.

6.4 Conclusion

We have presented in this chapter a drainage mechanism through the corner films. In order to be able to describe it, we have used a lubrication approximations which requires the relationship between the pressure gradients in both phases and the mean velocities. These relations were obtained by numerical solutions. These results are not restricted to the drainage problem, but generic to corner flows in square channels. Then, the pressure gradients are coupled through the laplace pressure due to the corner film curvature. Finally evolution equations are obtained through volume conservation.

When a flow rate is imposed in the inner non-wetting phase, the system of equations reduces to a single partial differential equation that describes the shape evolution of the corner films. Considering its application to the case of a trapped cluster, we show that the no-flux boundary conditions leads to a drainage of the films close to the cluster. We have calculated the delay time required to reach the pressure difference under which the cluster should shrink. It scales in Ca^{-2} if the cluster is located at the inlet, and in Ca^{-1} if it is located far from the inlet. Then the cluster should be drained through the corner film at a velocity that is proportionnal to the applied flow rate in the non-wetting phase. We note that it depends significantly on the viscosity ratio but the drainage flow rate is always much lower than that of the inner phase. Thus this process is slow. Interestingly, contrary to cluster mobilization by a viscous pressure difference between upstream and downstream the cluster that exhibits a threshold in the capillary number, the mechanism that we propose here applied even at very low Ca .

6.5 Summary

Flows in corner films

- In a square channel, the presence of wetting flows in the corners influences the main flow. The film size variations lead to pressure difference between the two phases.
- We model the flow in the framework of the lubrication approximation. We assume that the variation of the velocity field as a function of the direction of the channel are low compared to the one perpendicular at the flow. We write the mass conservation. Knowledge of the hydrodynamic resistances is required to obtain a relation between the two drops of pressure. We assume that the variation of the velocity field as a function of the direction of the channel are low compared to the one perpendicular at the flow. We calculate the hydrodynamic resistance as a function of the curvature radius of the corners for flat corners. When a flow rate is imposed in the inner non wetting phase, the system of equation reduces to a single partial equation. Considering the application to the case of a trapped cluster, we show that the no-flux boundary condition leads to a drainage of the films close to the cluster and thus to the drainage of the cluster.

Drainage of a trapped cluster through corner films

- Considering the application to the case of a trapped cluster, we show that the no-flux boundary condition leads to a drainage of the films close to the cluster and thus to the drainage of the cluster
- Numerical solutions of evolution of the corner films is discussed with boundary conditions of no flow rate at $x = 0$. Asymptotic solutions for long time and short time are obtained.
- The delay time required to reach the pressure difference required to under which the cluster should shrink scales as $1/Ca^2$ if the cluster is located at the inlet and as $1/Ca$ if it is far the inlet. We recall the the no-flux condition is imposed at the inlet.

Chapter 7

Experiments of drainage of trapped oil through corners films

In the previous chapter, we envisaged theoretically the possibility to drain a trapped cluster of oil by some flow in corner films. Briefly, if the displaced wetting phase has a low enough contact angle, it remains inside the wedge of channels although a meniscus is moving downstream. This corner films are in equilibrium, but their presence lead to a continuous flow of this displaced wetting fluid because of the viscous entrainment. Therefore, the size of the corner film decreases in time. Not only the wetting fluid occupying these films is progressively swept, but also any reservoir of this fluid trapped in capillary favorable regions. Indeed, the reduction of the corner film size increase laplace pressure, and thus the pressure difference between the two phase. When it is low enough, the blocked menisci around the cluster are no more stable and it empties. This process holds provided that the corner films form a continuous network and are connected to the clusters.

The aim of this chapter is to validate experimentally and quantitatively this mechanism, for various viscosity ratios and as a function of the capillary number. Apart from geometrical details, these are the two single physical parameters.

7.1 Experimental approach

7.1.1 Device and geometry

We need a geometry where it is possible to trap some wetting fluid by capillarity. One of the most simple geometry is a single derivation on a channel that has a smaller size, and thus a greater capillary pressure. The Figure 7.1 sketched the geometry of the device. Channels are of square cross section except in the narrow arm of the loop where the width is half of the height. The capillary pressure is thus higher in this arm by a factor of 1.5. As shown below, this difference is sufficient to provoke some phase trapping in this arm, for $Ca > 10^{-3}$.

The device was made either in PDMS either in SU8. The fabrication and the chip

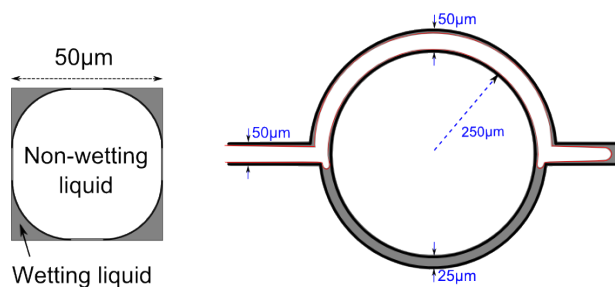


Figure 7.1: A schematic drawing of the circle channel zone, which is near the entrance of the SU-8 chip. The dimensions of this chip is $H = 50 \mu m$, $R_1 = 25 \mu m$, $R_2 = 12.5 \mu m$, $R = 250 \mu m$. The left one shows that the dark wetting liquid is in place and is pushed by the white non-wetting liquid. Because of this complete wetting system, the wetting liquid prefers to stay in the corners, as sketched in the right side (but the corner size is exaggerated).

characteristics have been presented in section 2.3. As compared to PDMS device, SU8 ones offer the great advantage that they are impermeable to oil. We will show in the following that it is a very important point.

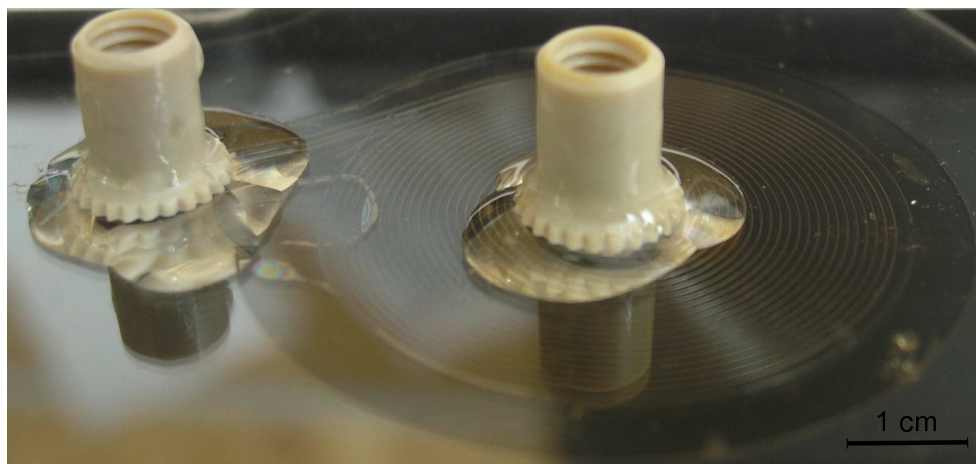


Figure 7.2: Image of the microfluidic chip made in resin SU-8. The resin is between two pieces of glass wafers. Two nanoports are bonded by a glue *épotecny* NOA61. The left one is the entrance and the right one is the exit.

In order to keep the meniscus inside the chip during the whole experiment and thus to ensure that the pressure difference between the phase remains at some values close to the capillary pressure, we specially design a very long channel in this chip, using a spiral that could be seen in Figure 7.2. The total length is about $1.41 m$, which allows to obtain very long resident time at low flow rates.

The inlet and outlet connexion are made using nanoports: the one in the center of spiral zone is the outlet, the other one, which is connected with the linear branch, is the inlet. At the inlet side, a switchable valve of is connected between the seringe and the

inlet, which allows to fill the device with the wetting fluid and then to switch easily to non-wetting fluid to begin the experiment.

7.1.2 Capillary trapping

The geometry that we used is naturally designed to ensure a wetting phase trapping. Before focusing on the drainage through the corner films, let us analyze the invasion of this particular device by a non-wetting fluid.

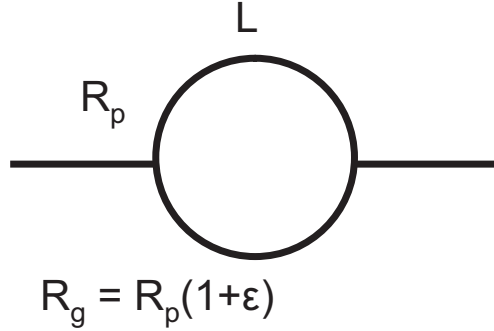


Figure 7.3: The considered geometry with two section radius lightly different from each other. L is the circle length. R_p and R_g are the radius for the narrow and large branches, where $R_g = R_p(1 + \epsilon)$.

We consider the model geometry depicted in Figure 7.3, consisting in a loop with two arms of different sectional radii. At low capillary numbers and in a flow rate imposed experiment, the non-wetting fluid enters only the largest channel. The other meniscus is blocked by capillarity. When the meniscus in the larger channel has reached the next junction, the remaining wetting fluid remains trapped. In order to determine the capillary number below which this trapping occurs, it is convenient to consider the time at which the meniscus in the larger channel as that to invade the whole arm of the loop. The mean velocities in the large and narrow channel (v and v' , respectively) are given by

$$v = \frac{\alpha a^2}{\eta_1 L} (P - \gamma C) \quad (7.1)$$

$$v' = \frac{\alpha' a'^2}{\eta_2 L'} (P - \gamma C') \quad (7.2)$$

where the prime symbol stands for the narrow channel, a is the channel size, L is the channel length, α the hydrodynamic conductance factor ($\alpha = 0.035$ for a square channel), P the pressure difference between the two junctions, and C is the $C = 1/(1/R_1 + 2/H) = a/4$.

The fact that the meniscus in the narrow channel is blocked ($v' = 0$) allow to obtain directly the critical capillary number Ca_c below which complete trapping occurs. One obtains

$$Ca_c = 4\alpha \frac{a}{L} \left(\frac{a}{a'} - 1 \right) \quad (7.3)$$

The term a/a' is the ratio of channels' arbitrary shape.

For our geometry, $a/a' = 3/2$ and we find a value of for the critical capillary number of 4.4×10^{-3} . For Ca above this value, the wetting fluid is partially trapped in the narrow side. Pratically, the partial trapping play an impotant role when $Ca > 2 \times 10^{-2}$. Because the partilly trapped zone is till limited compared with the whole volume, as shown in Figure 7.4. A trapping is also performed in the experiments. So all our measurement are taken with $Ca < 2 \times 10^{-2}$.

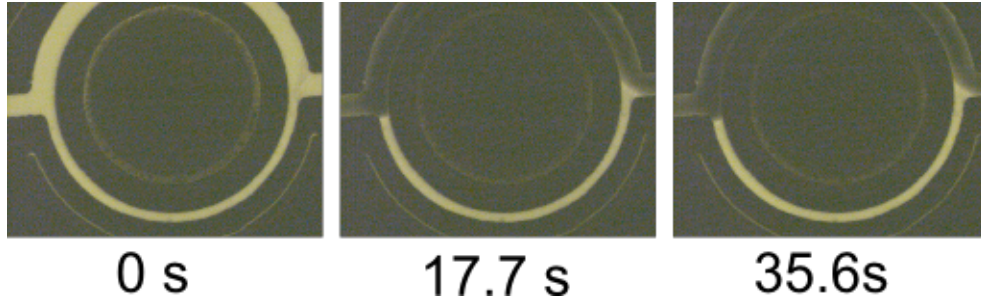


Figure 7.4: The partial trapping occurs for $Ca > Ca_c$

7.1.3 Fluids and materials

The device are in made in two different materials. PDMS and SU8 are used. Section 2.3 details the fabrication procedures.

We use several couple of fluids of various viscosity ratii that are in a total wetting situation. The Table 7.1 lists these. Part of the experiments are carried out under a binocular Olympus SZX16 using a standard transmitted light for illumination. A camera AVT Pike F505B allow to record movies. In this case, the two liquids are distiguinshed by their refraction index.

In the two last systems in Table 7.1 a fluorescent dye *KeyStone yellow 131SC* as been dissolved in dodecane to allow fluorescence intensity measurement using darkfield fluorecent microscroscopy. A olympys microscope with a $10\times$ objective has been used for this purpose. The main interest of fluorscence microscopy is here to achieve an estimation of the volume of wetting liquid inside the corner films.

7.1.4 Protocol

The following protocol has been systematically used in the experiments.

The experiments begins with filling the whole channel by the wetting liquid (here, we use dodecane). The flow comes from the outlet side at a flow rate of about $300 \mu L/h$, controlled by a seringue pump. The wetting fluid is pushed during a rather long time (30 mins) to remove any bubble or drops that could be formed during this filling. After this stage, the whole device and the tubing is entirely filled with the wetting fluid.

in SU8 device	$M = \eta_1/\eta_2$	P_{Ca2} (Pa)	γ (mN/m)
FC-40/silicone oil V5	0.75	150	2.50
FC-40/dodecane	2.53	305.3	5.09
FC-72/silicone oil V20	0.03	265.2	4.42
FC-40/dodecane (fluorescence)	2.53	187.8	3.13
FC-70/dodecane (fluorescence)	17.9	259.2	4.32

Table 7.1: Parameters of used complete wetting systems in the microfluidic chip of resin SU-8. In the PDMS chip, FC-40/silicone oil V5, and FC-40/silicone oil V20 are used. A vast variation of M is tested in our systems. The capillary pressure of the narrow channel P_{Ca2} indicate the pressure necessary to push the non-wetting liquid into it. It is calculated by $P_{Ca2} = \gamma(1/R_2 + 2/H)$, where f and H are the largeur and height of the narrow channel.

Then the outlet tube is unplugged from the syringe and immersed inside a vial containing some wetting fluid.

The final step corresponds to the measurement one. The tubing at the inlet is plugged to a syringe containing the non-wetting fluid and a fixed flow rate is applied. We varied this flow rate in several order of magnitude as it is the main control parameter. Time zero is set at the time at which the meniscus separating the two fluids enters the device.

7.2 Experimental results

We start by the results obtained in SU-8. Indeed as will be shown in the following, the experiments in PDMS should be analyzed with great care due to oil permeation in the PDMS.

7.2.1 Qualitative observations

Let us first describe qualitatively the observations. As chown in the serie of images in Figure 7.5, the invading fluid (in dark on the images) invades only the large arm of the loop at low capillary numbers. Then, after some time, the wetting fluid trapped in the narrow arm (called "tarpped cluster" in the following) starts to be drained progressively. Interestingly, both upstream and downstream menisci recede at the same time: the cluster shrinks very slowly. This SU8 resin is impermeable with respect to the fluids used, the fluids is drained through the corner films.

The dynamics of this drainage exhibits two phases. At first, the menisci of cluster do not move (or very slightly) during a period of time, in the following which refers to the delay time. Then the drainage occurs at a constant speed. The duration of this second phase is generally on the same order of magnitude as the first one.

In the framework of the theoretical analysis of the previous chapter, these two phases are rather straightforward to understand. Just after the trapping, the size of the corner film is fixed by the moving meniscus and equals to $1/4$ of the channel width. The pressure

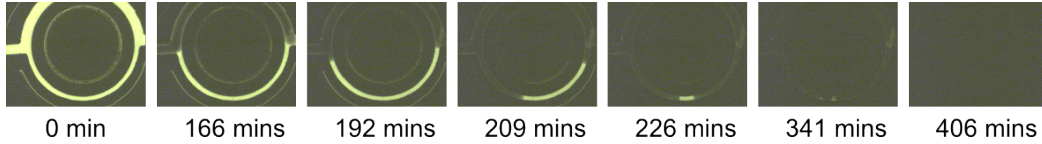


Figure 7.5: Drainage process of a complete wetting system: FC-40/dodecane (fluorescence)/SU-8. The whole circle channel is filled by a fluorinated liquid (dodecane). The non-wetting liquid is pushed in from the left side with $Ca = 1.2 \times 10^{-3}$. The wetting fluid in the narrow channel is trapped in the beginning, and then drained through the corner of the rectangular channels. The intensity of fluorescence shows the wetting liquid volume variation.

difference between the two phase is too low to allow the menisci to enter the narrow channel. Then, after some time, the drainage of the corner film leads to a reduction of the corner film size around the cluster. At a given size threshold, the pressure difference reaches the capillary pressure of the narrow channel, allowing the menisci to enter it.

7.2.2 Estimation of film size variations

In order to be more quantitative, we use fluorescence microscopy to estimate the corner film size. For low enough dye concentration and illumination intensity, the fluorescence intensity is proportional to the dye quantity. Under this assumption, it is thus proportional to the volume of the corner film.

We choose a rectangular zone $\Omega(x, y)$ which contains the channel wall of large channel side and shown in the insert of Figure 7.6, where we see a corner film. We compute a normalized corner film intensity $I(t)$ by integrating the pixel intensity over this domain, defined by

$$I(t) = \frac{I(t) - I_{min}(t)}{I_{max}(t) - I_{min}(t)} \quad (7.4)$$

where $I(t)$ is the mean intensity on the chosen domain.

An example of this fluorescence intensity variation is shown in Figure 7.6. Three regimes could be observed (see T_1 , T_2 and T_3 in the figure). By correlating this regime to the cluster menisci movement, we are able to interpret these regimes.

1) Initial delay. At first, the intensity decrease which means that the corner wetting volume decreases. Correlatively, we observe that the mensici around the trapped cluster are blocked. They do not move or adjust in the junction. In the beginning, when the cluster is created, the local pressure difference between the two phases $\Delta P_1 = P_1 - P_2 = \gamma(1/R_1 + 2/H)$, where $R_1 = H/2 = 25\mu\text{m}$. The pressure difference necessary for the non-wetting fluid to enter the narrow channel is $\Delta P_2 = \gamma(1/R_2 + 2/H)$, where $R_2 = 25\mu\text{m}$. Since the corner film size is decreasing, the pressure difference increases and eventually reaches ΔP_2 so that at the end of this first regime, the non-wetting fluid enters the narrow channel. Both upstream and downstream menisci advances.

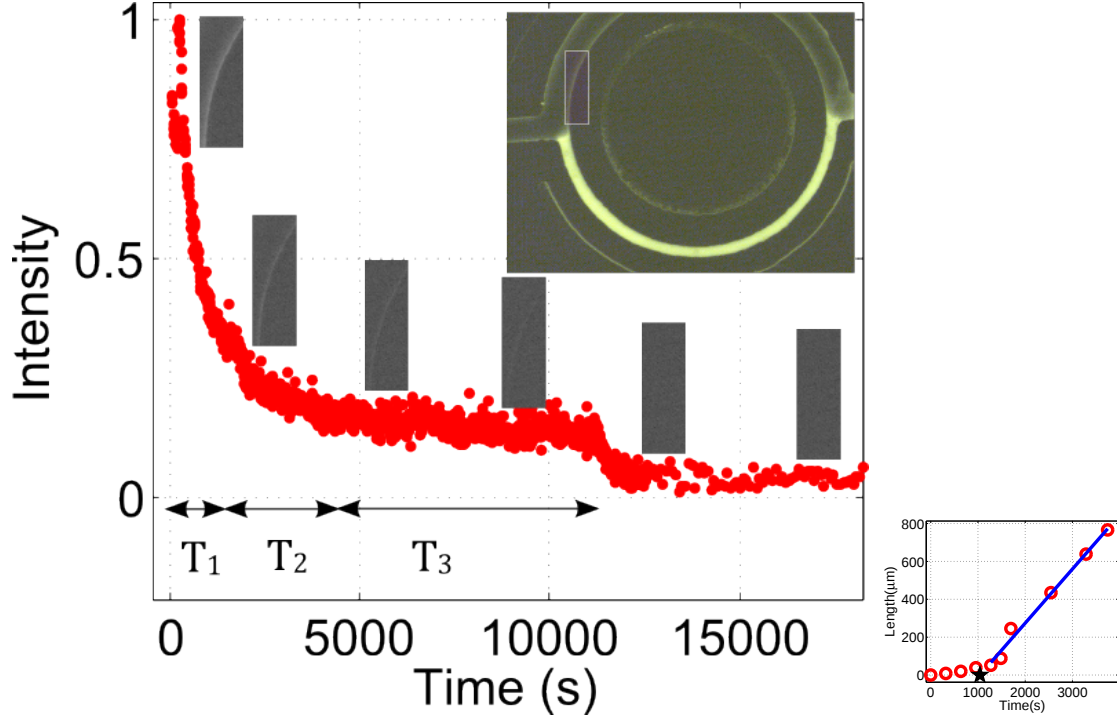


Figure 7.6: Normalized total intensity of fluorescence in the chosen rectangular in the insert photo, for an experiment conducted at $Ca = 1.2 \times 10^{-3}$, with the FC-40/dodecane/SU8 system. The intensity variation indicates that the wetting liquid volume in the corner film decreases with time. Three periods T_1 , T_2 and T_3 correspond to the drainage initial delay, the drainage of the cluster, and finally the drainage of corners.

2) Drainage of the cluster. During this regime, fluorescence intensity measurements show that the volume of the corner film is fixed. At the same time we observe a slow movement of the menisci leading to a drainage of the trapped cluster. Once the non-wetting liquid enters the narrow channel, the advancement in this narrow channel asks for the same local pressure difference ΔP_2 . Since we expect the drainage occurring in the corner films to be rather slow, the menisci move very slowly, meaning that the pressure difference between the phases remains equal to ΔP_2 . This is consistent with the observation. In other words, the boundary conditions is switched from no flux to a fixed corner film size at the transition between the two first regimes.

The fluorescence intensity in this plateau is around 20% of the initial intensity. Recalling that the corner film size is directly related to the pressure difference, we expect the ratio of the film size in the plateau to the initial one to equal $\Delta P_1/\Delta P_2 = 2/3$, given the geometric features of the device. Since the intensity is related to the volume of the wetting fluid in the corners, we would expect a value of about 44% in this plateau, under the assumption that the fluorescence intensity is proportional to the dye quantity. Since many phenomena could affect such a linearity, it is not surprising to obtain a quantitative discrepancy. In these experiments, we could only interpret qualitatively the intensity variations.

3) Drainage of the corner film. At the end of the second regime, the trapped cluster is totally drained, except along the corners. At this time, the fluorescence intensity decreases again, meaning that the corner film size decreases again. Since there is no more a reservoir of wetting fluid in the trapped cluster, the boundary conditions upstream switches to no flux again, and leads to a drainage of the corner film.

7.2.3 Cluster length measurements

Since it is not straightforward to achieve a quantitative measurement using fluorescence microscopy, we limit ourselves to measure the size of the trapped cluster as a function of time. More precisely, we compute through image analysis the length variation of the trapped cluster, $\Delta L = L(0) - L(t)$. Since the channel has a constant cross-section, this measurement is also a measure of the drained volume. Figure 7.7 displays an example of this analysis. We recover the two first regimes described above. In the first one, $\Delta L \approx 0$ and in the second one, it increases linearly with time. Depending on the experiments, the length variation does not exactly vanish during the whole first regime. This is due to a progressive adaptation of the meniscus curvature inside the junctions. Since it is related to details of the geometry of the junctions, we do not discuss further this effect and restrict ourselves in the following to measure systematically the two accessible quantities of the length variation as a function of time: the duration T_1 of the first regime, and the drainage flow rate given by the slope of $\Delta L(t)$ in the second regime times the cross section area. These two quantities will be compared to the theoretical analysis in the following.

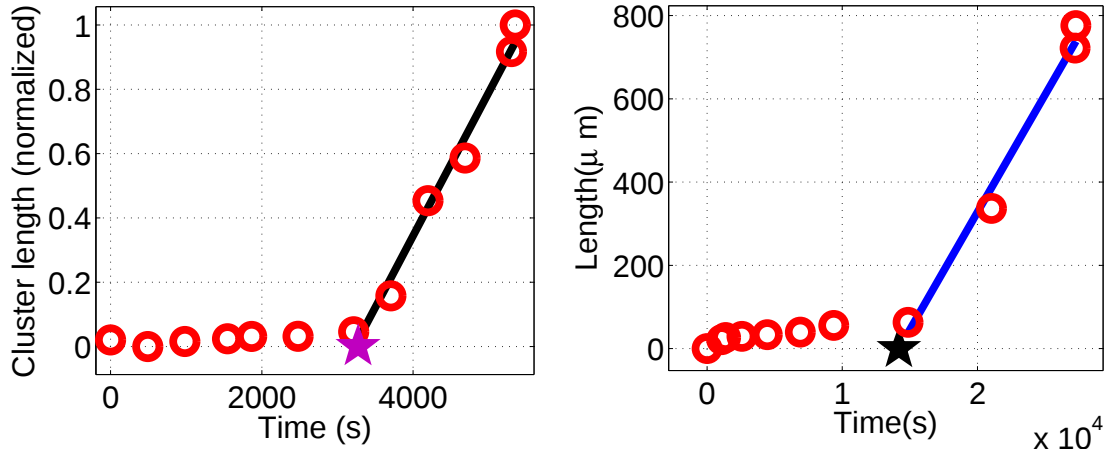


Figure 7.7: Two examples of normalized or real cluster length variation of the trapped cluster.

7.2.4 Delay time before drainage

We report in Figure 7.8 the delay time measured systematically on various systems as a function of Ca . this time has been determined by plotting the cluster length as a function

of time and by defining the transition between the first two regimes (see Figure 7.7). The data could be divided into two groups. At low Ca the delay times are, though dispersed, described by a power-law of exponent -1, *i.e.* $T_1 \sim 1/Ca$. At first sight, the viscosity ratio does not have a strong influence. At high Ca ($Ca > 10^{-2}$), we observe an abrupt decrease of the delay time. However, the scenario is somewhat different in this case, since we approach the limit at which the viscous forces are too strong to provoke the capillary trapping. Indeed, as explained in Section 7.1.2, trapping occurs only below a critical capillary number that is on the order of 4.4×10^{-3} . The scenario is therefore different for this data, since drainage occurs not only because of the corner films but also because of the high pressure drop. In the following, we focus on the data obtained at lower capillary numbers.

Let us now compare these results to the prediction of the previous chapter. As discussed in Chapter 6, we expect two different regimes for the delay time. If the cluster is located very close to the inlet, then the delay time is simply the time required to reach the critical corner film size. Then the expected scaling is $T_1 \propto Ca^{-2}$. If the meniscus is located far from the inlet, the delay time is much higher and the scaling switch to $T_1 \propto Ca^{-1}$. The transition between these two regimes depends on Ca and is given by $Ca_c = 4.4 \times 10^{-3}$. For the geometry used in our device, the distance x_c separating the inlet and the cluster is about 1cm, that is to say $\tilde{x}_c = 200$. Thus, for the range of studied Ca , we expect to be always in the second regime, where the delay time is inversely proportional to Ca . This is what we get experimentally on about two orders of magnitude, as shown in Figure 7.8.

In order to achieve a quantitative comparison, we replot in Figure 7.9 the data in the normalized units of the theoretical part. Concerning the delay time, these are normalized by $\eta 2a/\gamma$. In these units, the prefactor of the Ca^{-1} scaling depends on M and of the value of ϵ_c , the corner film size at which the cluster starts to be drained. For the value of ϵ_c corresponding to the geometry of the device, which is $1/6$, we compute the theoretical delay time for several values of M . They are plotted together with the experimental data in Figure 7.9. For several systems the agreement is rather good, given that there is no fitting parameter. Putting aside one of the systems (FC-40/dodecane), the increase of the delay time when increasing M is experimentally consistent with the expected variation. We do not understand why this particular system is so different from the other and gives the delay times that are more than one order of magnitude than expected.

7.2.5 Drainage flow rate

From the measurement of the cluster length in time, we determine the flow rate Q_d at which the cluster is drained. For $t > T_1$, the cluster length as a function of time is fitted by a linear relation which, multiplied by the channel cross-section $2HR_1$, leads to the drainage flow rate Q_d . Since the theoretical analysis predict that during this drainage the mean velocity in the corner films is simply proportional to the velocity in the inner phase, we expect Q_d to be proportional to Ca , or in other words to the imposed flow rate Q_i . Thus we plot in Figure 7.10 the ratio Q_d/Q_i as a function of the capillary number. Although the points are rather dispersed, this ratio remains roughly constant in the range of capillary

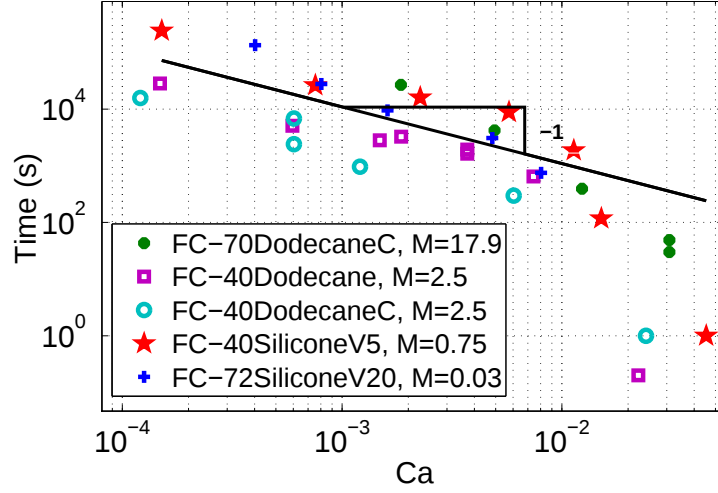


Figure 7.8: Delay before the drainage of cluster starts for systems of various viscosity ratio, in SU-8 device. The solid line is an indicative power-law function of exponent -1.

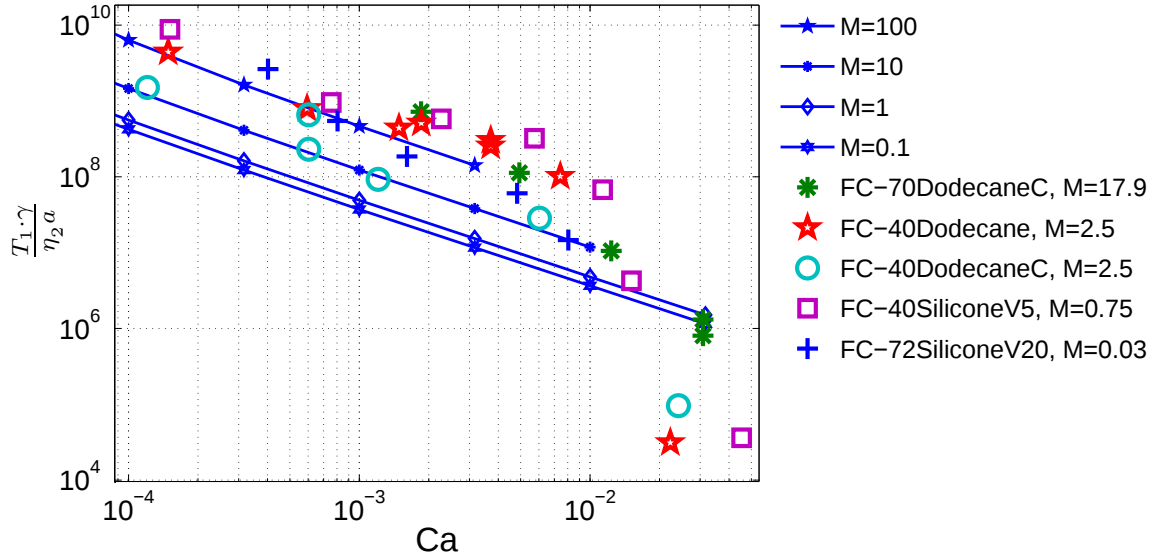


Figure 7.9: Various complete wetting systems with different viscosity ratios M . The values are shown in Table. 7.1. All the systems verify the relation $T_1 \propto Ca^{-1}$. M leads to light variations, but T_1 depends mainly on Ca .

number tested, as expected. It increases when increasing the viscosity ratio. This effect could be understood easily since the drainage flow rate is simply the consequence of viscous entrainment by the inner phase. The more viscous the inner phase is, the more efficient the drainage takes place.

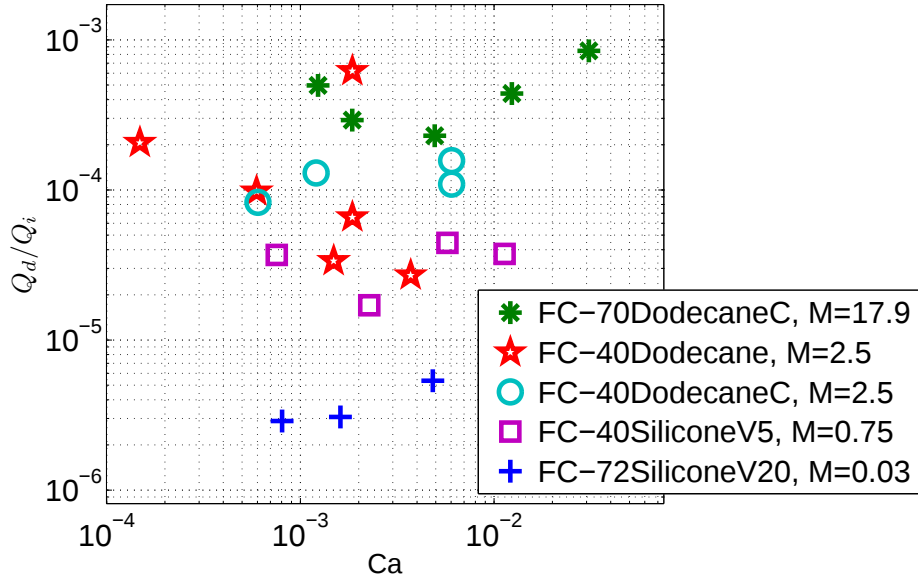


Figure 7.10: Drainage flow rate of the cluster normalized by the imposed flow rate Q_d/Q_i , as a function of the capillary numbers. For various systems, this ratio is in a first approximation independant on the capillary number, showing that $Q_d \propto Ca$.

In order to analyze further the effect of the viscosity ratio, we plot in Figure 7.11 the ratio as a function of M . We recall the theoretical prediction detailed in Section 6.3.7.1 :

$$Q_d = c\epsilon_c^2 M f(\epsilon_c, M) Q_i. \quad (7.5)$$

This M dependency of the flow rates ratio Q_d/Q_i is not trivial but since f is constant in the limits of small or big M , it increases proportionally to M in these limits. The predicted relation is plotted together with the experimental results in Figure 7.11, for the experimental value of ϵ_c ($2/3$). The comparison is not very accurate, but the global trend is on rather good agreement. The order of magnitude is roughly predicted, but the measured values are for some system higher than that of the model, by a significative factor.

7.2.6 Results in PDMS chips

We now present the results obtained in PDMS chips. The observations are qualitatively the same: there is a delay before the mensici enters the narrow arm of the loop. This delay time is plotted in figure 7.12 as a function of the capillary number. When comparing the rescaled time to the theoretical ones, we find that experimental times are much lower than predicted. Such a discrepancy falls out of experimental errors and uncertainties. Furthermore, the dependency of this time as a function of Ca is also different to that predicted. We find that below 10^{-3} , it is roughly independant on the applied capillary number. Since the experiments conducted in SU-8 device lead to delays on the order of

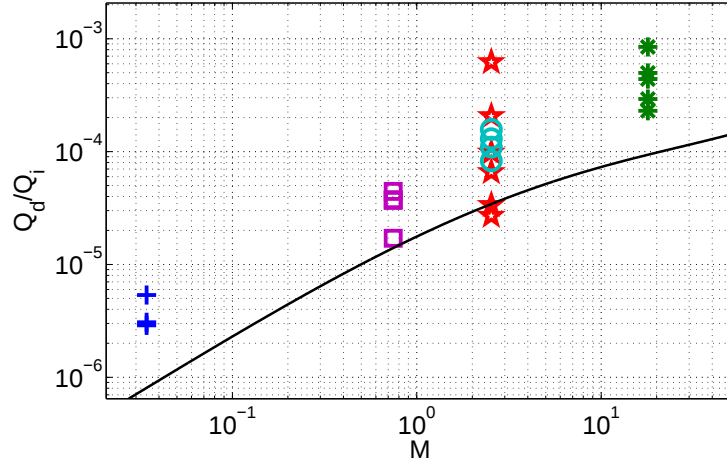


Figure 7.11: Comparison between the experimental drainage rates (normalized by the imposed flow rate) Q_d/Q_i and the predicted ones (solid lines, see text), as a function of M . The data are the same as in figure 7.10, and stand for various flow rate. Their dispersion is an indication of the error bars, which are rather high in these experiments.

the predicted one and decreases as Ca^{-1} , we can conclude that a different mechanism is occurring in PDMS device.

A possible interpretation of this result is to consider that PDMS is permeable to oil. The oil cluster is progressively swelling the PDMS. This hypothesis is rather consistent with the fact that the observed time is in a first approximation independant on the capillary number.

This result has some important consequences. It illustrate that PDMS could not be used to study biphasic flows when the time scale of the experiment is higher that a few dozens of seconds. This is particularly the case of drainage or imbibition experiments in micromodels of porous media. We believe that this result prevent to interpret the perfect sweeping that is observed at long times in these types of experiment.

7.3 Discussion

The experimental results presented above capture well the trends predicted in the previous chapter. The mechanism seem to be rather robust: the scaling are recoverd, the order of magnitude is correct. A quantitative agreement is even found for some systems, but it is necessary to recognize that the data are globally dispersed and that a rather important disagreement that is found for some systems. Although we feel comfortable concluding that the mechanism we propose for the corner film to be drainged holds, we are wondering why the agreement is not better, and why there is an important data dispersion. Several points might be raised.

Firstly, these experiments are rather long : up to a day for the lowest capillary numbers. At these time scales, many external parameters could vary significantly, the temperature

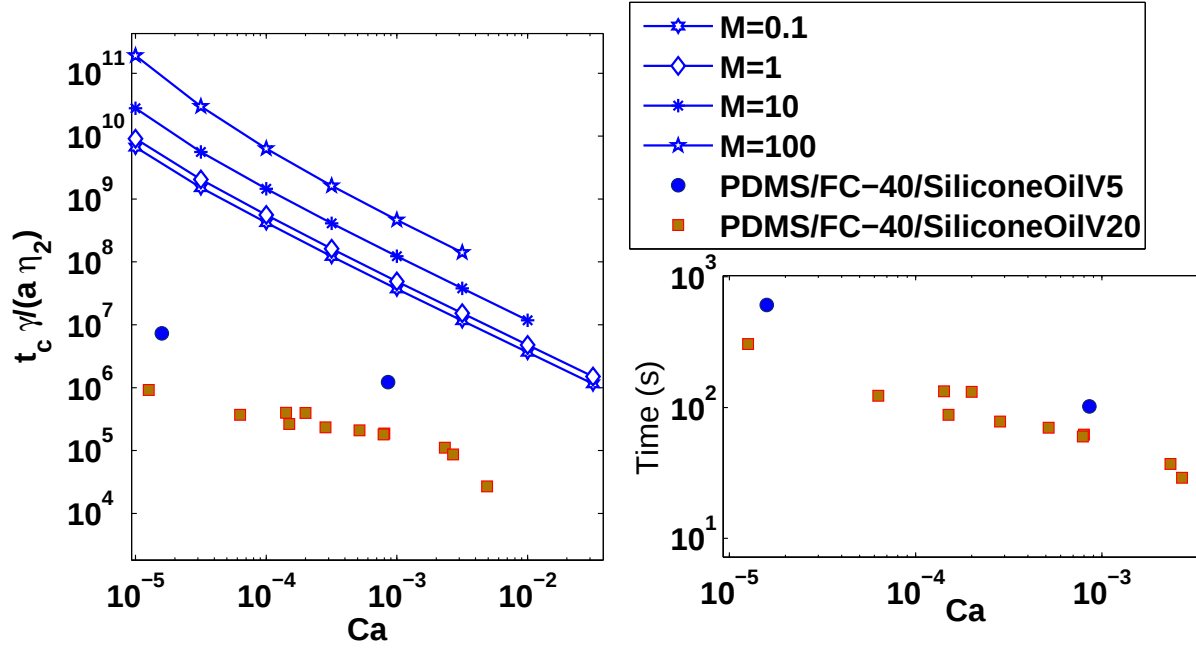


Figure 7.12: Delay time before drainage inside PDMS devices. The left plot displays the normalized experimental times T_1 as a function of the capillary numbers, together with the theoretical calculated times (M between 0.01 and 100). On the right, the same data are plotted in physical units.

in particular. A more controlled environment seem to be necessary to achieve a better accuracy.

Secondly, and probably the main point, the delay time is greatly dependant on the exact nature of the boundary conditions. In particular, it is experimentally very difficult to achieve a no-flux boundary condition at the inlet. We use a tubing that is not wet by the wetting fluid. Thus, we expect the tubing to be completely filled by the non-wetting fluid when the experiments starts. However, it is not possible to prevent the wetting fluid to form some small droplets or to be trapped in the inlet region of chip. Indeed, at this position, the geometry is not well controlled. And although the nanoport connection is optimal concerning dead volumes, the junction between the tubing and the chip is possible to trap a small amount of the wetting fluid. We could not easily verify this issue since the glue at the inlet make the observation difficult. If there is an - even small - reservoir at the inlet, then the no-flux boundary conditions at the inlet is not satisfied at the beginning of the experiment. An additional delay can occur. In some experiments, we have seen some droplets of the wetting fluid flowing just after the meniscus has passed the junction. These experiments were discarded but they underline that there might be some wetting fluid trapped at the inlet. We believe that one of the only way to remove this experimental difficulty would be to use a device where the wettability is different close to the inlet.

7.4 Conclusion

We have presented in this chapter the experimental results that validate a drainage mechanism through corner films. The qualitative observations are in very good agreement with the theoretical predictions presented in the previous chapter. The drainage of a cluster of wetting fluid trapped by capillarity is delayed from the invasion by the non-wetting fluid. This delay time corresponds to the time necessary to decrease the corner film size up to a value set by the capillary pressure difference between the moving meniscus and the one inside the trapped cluster. In practice, this time corresponds to the time required for the film size variation to arrive to the cluster position. It leads to a scaling in Ca^{-1} that is verified experimentally. Moreover, the prediction succeeds in accounting for the order of magnitude of this delay time and for the variations with the viscosity ratio, though for some series of experiment, a rather important dispersion is found. After this delay time, the cluster empties, and the corner film size near the cluster remains constant until it is completely swept. Again this matches the predictions. We were able to measure the drainage rate. We find that it is roughly proportional to the capillary number in the low Ca limit. The order of magnitude of this flow rate is again well captured by the theoretical analysis. It is very low since the ratio of the drainage flow rate to the imposed one is between 10^{-6} and 10^{-3} , depending on the viscosity ratio. The higher M is, the higher the drainage flow rate.

The mechanism of drainage through is thus very slow as compared to standard drainage due to cluster displacement under viscous pressure drops. It is not likely to be suitable for oil recovery applications since in these applications, the length scale is huge and recovery time scales are on the order of years. However this mechanism might be used in other applications that involve porous media on much shorter length scale such as soil remediation.

Beside, this experimental study shows that PDMS devices are not suitable for biphasic flows involving long time scales due to oil swelling of PDMS.

We have studied systems that are in complete wetting situation. Corner films are also present in partial wetting conditions, when the contact angle is low enough. It would be very interesting to see whether under the partial wetting situation, this drainage mechanism still occurs. Although there is in principle no main differences, the contact angle hysteresis may complicate the size variation of the corner films.

Finally, we investigated a drainage situation, but the case of imbibition might also be interesting.

7.5 Summary

Experimental approach

- A microfluidic dispositif of resin SU-8 is designed to study the consequence of corner flows in drainage process. We focus on the complete wetting situation.
- A general discussion about the capillary trapping as a function of capillary number is presented. We are interested in the trapping situation with an important volume under complete wetting condition. After percolation, these clusters are connected through the corners and could be displaced entirely.

Experimental result

- The whole drainage of cluster is characterized quantitatively. We analyze the delay time before drainage and the drainage flow rate. A quantitative agreement between the data and the model is displayed.

Conclusions and Perspectives

Rhodia company has developed in the last five years an activity dealing with chemical enhanced oil recovery. Chemical compound enhance oil recovery because they increase the viscosity of water, decrease the interfacial tension or change the wetting conditions. In this work, we deal with the last topic. Our aim is to understand at the pore level the role of the wetting properties on the displacement of oil and on its trapping.

We focused on a simple geometry: a capillary tube. We take advantage of microfluidic and millifluidic technologies and prepare geometries of various shapes (circular or rectangular) in various materials (PDMS, SU8, glass). We use various surface treatments to control the energy of the surface and tune the wetting properties. We followed the displacement of the interface between the two phases in various wetting situations: complete, partial, pseudo-partial. Pseudo-partial situation that corresponds to a positive spreading parameter and to a positive Hamaker constant is an exceptional situation for air liquid systems. We have shown that at the opposite it is a common one for liquid/liquid systems as soon as the solid surface is coated with a hydrophobic layer. This situation is likely to happen in the oil well where the hydrophilic rock is covered by an asphaltene layer. In circular channel, the displacement of the meniscus in the three situations may be described using the thermally activated depinning theory. Our experiments deals with the low capillary number regime and hydrodynamic effects play no role. Thermally activated depinning theory assumes that the contact line moves through a succession of jumps. Two parameters describe the pinning depinning events: E^* , the typical energy barrier between two pinned configurations of the contact line and λ the size of the jumps.

We show that the partial case corresponds to high energy values ($120 k_B T$), where as the pseudo-partial case corresponds to low energy values ($40 k_B T$). The size of the hysteresis plateau is correlated to the normalized energy suggesting that the displacement occurs through a succession of jumps between pinned configurations. Larger values of the correlation length are measured for pseudo-partial case with low hysteresis plateau. This comforts the previous picture, lower hysteresis suggests the presence of less defects and thus of larger distance between two jumps.

Pores in the reservoir are not circular. Wetting fluid remains prisoners in the corners. We have analyzed the role of the flow in the corners and shown that they modify the value of the apparent capillary pressure. In other words, zero velocity occurs in the invading fluid not for a zero pressure drop for the internal fluid but for an negative (or positive) pressure drop balanced by a positive (or negative) pressure drop in the corner flows. This implies

that the drop of pressure $P_1 - P_2$ where P_1 is the pressure of the invading fluid near the inlet and P_2 the pressure of the prisoner fluid near the outlet is not equal to the capillary pressure γC , where C is the curvature of the meniscus and γ the interfacial tension. These corners flows have a huge repercussion in absence of reservoir for the wetting phase. Flow in the invading phase sweeps the liquid in the corner. The shape of the corner changes due to mass conservation and the curvature radius decreases. A meniscus blocked near a small throat will thus enter it when its size will fit it. We have developed a model in the lubrication framework to describe this process. The resulting set of equation is a Burger equation remembering the equation of drainage in foams. Using Comsol, we have calculated the values of the velocity and of the hydrodynamic resistance. Experimental data agree quantitatively with the experiments.

The outlook of this work deals with this last point. We have pointed out a new process that modifies the drainage and the oil trapping mechanism and induces a new mechanism of oil recovery. We note that this mechanism is very efficient. No oil remains trapped. We have only studied its pertinence in the complete wetting situation. Experiments dealing with in the partial wetting situation are required.

From an application point of view, we have to check the pertinence of this process in more complex geometries. We also note that this process this process supposes the use of high volumes of invading phase and the existence of wetting films. These constraints might be too strict for the oil enhanced recovery applications.

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