

Wetting on heterogeneous metal-oxides regular patterned surfaces by a non-reactive liquid metal Moustapha Diallo

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Wetting on heterogeneous metaloxides regular patterned surfaces by a non-reactive liquid metal

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École doctorale n°579 : sciences mécaniques et énergétiques, matériaux et géosciences (SMEMAG) Spécialité de doctorat : Sciences des Matériaux

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NOMENCLATURE

Latin letters

Α	Surface area	m^{-2}
a (d)	Pattern size	m
a ^s	Puissance law	
A _{drop}	Contact area of the drop	m^2
C _{mp}	Fitting constant	
CS	Cylindrical pillars in square arrangement	
CH _{reg}	Cylindrical pillars in regular hexagonal arrangement	
CH _{irreg}	Cylindrical pillars in irregular hexagonal arrangement	
D	Drop diameter	m
d_s	Diameter of the sphere	m
D_c	Critical diameter of the drop	m
D^l	Diameter of the solidified drop in lateral view	m
D^t	Diameter of the solidified drop in top view	m
d1 (d2)	Spreading direction of the triple contact line	
d_m	Molecular dimension	m
Ε	Energy	J
E _{diss}	Dissipated energy	J
F	Force	Ν
f , f_s	Surface fraction or Cassie fraction	
F_H	Helmholtz free energy	J
F_P	Pinning force per unit length	$N.m^{-1}$
G	Gibbs free energy of the system	J

g	Gravity	$m. s^{-2}$
G_f	Geometric factor of the pillars	
G _{drop}	Position of the centre of the drop	pixels
Н	Reduced contact angle hysteresis	
h	Texture (or pattern) height	m
H _d	Maximal height of the drop	m
h _d	Drop thickness	m
k _B	Boltzmann constant	$J. K^{-1}$
L	Liquid phase	
m_{Pb}	Mass of the lead drop	kg
Ν	Number of molecules	
n _d	Number of defects per unit area	m^{-2}
n_p	Number of pixels	
Oh	Ohnesorge number	
Р	Pressure	$N.m^{-2}$
P_I	Impact number	
ps _{im}	Image scale	pixels/mm
р.	Pinning effect	
R	Surface or contact radius	m
r _a	Average surface roughness	m
Re	Reynolds number	
r_W	Surface roughness or Wenzel roughness	
S	Solid phase	

S	Distance between pillars of the texture	m
spl.	Drop splitting	
S _w	Wetting parameter	$N.m^{-1}$
sf _{pack}	Packing limit	
SS	Square pillars in square arrangement	
SH _{reg}	Square pillars in regular hexagonal arrangement	
SH _{irreg}	Square pillars in irregular hexagonal arrangement	
Т	Temperature	K
t	Spreading time	S
t _i	Inertial time	S
t _{fall}	Fall time of the drop	S
t^a_{satb}	Stabilization time of drop contact angle	S
t^a_{satb}	Stabilization time of drop contact diameter	S
TCL	Tripe Contact Line	
U	Spreading velocity of the triple contact line	$m.s^{-1}$
V	Vapour phase	
V ₀	Impact velocity of the drop on the solid surface	$m. s^{-1}$
V_L, V_{drop}	Drop or liquid volume	m^3
V _{fall}	Average velocity of the dispensed drop	$m.s^{-1}$
V_u	The unsupported volume	m^3
W	Work	J
We	Weber number	
x	Small displacement of the triple contact line	m

Ī	Position of the drop center of mass	m
Z _{CM}	Altitude of the position of the drop center of mass	m
Greek le	etters	
α_{cam}	Tilted angle of the camera	o
α_{mp}	Fitting parameter	
α_{TCL}	Tilted angle of the triple contact line	o
β	Slope angle of the solid surface	o
γ , γ_{LV}	Surface tension of the liquid drop	$N.m^{-1}$
γ_{SL}	Surface tension of the interface solid-liquid	$N.m^{-1}$
γsv	Surface tension of the interface solid-vapour	$N.m^{-1}$
δ_p	Maximum drooping depth	m
$\Delta \theta$	Contact angle hysteresis	o
8	Hypothetical displacement of the TCL	т
E _{el}	Elastic energy	J
$ heta\left(heta^{st} ight)$	Apparent contact angle	٥
θ_a	Advancing contact angle	o
θ_{C}	Cassie contact angle	o
$ heta_E$	Equilibrium contact angle	o
$ heta_L$	Left contact angle of the drop	o
θ_r	Receding contact angle	o
$ heta_L$	Right contact angle of the drop	o
θ^L	Contact angle of the solidified drop in lateral view	o
θ^t	Contact angle of the solidified drop in top view	o

θ_W	Wenzel contact angle	o
$ heta_Y$	Young contact angle	o
κ^{-1}	Capillary length	m
k _B	Boltzmann constant	$J. K^{-1}$
Λ	Contact line density	m^{-1}
λ	Feature size of the texture	m
μ	Dynamic viscosity of the fluid	Pa.s
λ_a	Average wavelength of asperities	
λ_i	Linear fraction	
ρ	Drop density	$kg.m^{-3}$
$ au^*$	Spreading time	S
$ au_r$	Characteristic time of the first receding	S
Ψ_{diff}	Set of pixel in the symmetrical difference	
Ψ_{drop}	Set of pixel in the drop contact surface	
Ψ_{cth}	Set of pixel in the optimal circle	

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Introduction

Wetting is a common phenomenon in industrial processes where a liquid is brought into contact with a solid surface, including coatings, drying, cleaning, painting, adhesion, solidification and galvanization.

The latter is a process that protects industrial steel sheets against corrosion. This protection is provided by a thin layer of zinc alloy obtained by immersion into a liquid bath. During this immersion, the zinc liquid must wet the steel for the most uniform coating. The steel sheet is then removed from the bath by entraining a layer of zinc liquid. Before immersion in the zinc alloy bath, the steel sheets are annealed at temperature of more than 750°C in a reducing atmosphere composed of nitrogen and hydrogen. This annealing has two main objectives: the recrystallization of steel sheet and the reduction of surface oxides.

The recrystallization of steel eliminates strain hardening from cold rolling and thus improves the formability of steel sheet. The reducing atmosphere reduces surface iron oxides and thus promotes good wetting by liquid zinc.

However, the new steel sheets contain addition elements with higher contents. These so-called high yield strength steels, both high strength and good ductility, are intended to reduce the mass of car body.

On the other hand, the less-noble elements such as silicon and manganese in the steel sheet diffuse to the surface during the annealing process to form oxide particles or films. These oxides do not promote the wettability of the steel sheet and can lead to defects in the quality of the final coating.

To study the influence of these oxides on wetting, several authors studied the wettability of binary alloys of iron after annealing (Fe-Si [1], [2]).

In these studies, iron alloys first undergo an annealing process. Then different oxides of addition elements are obtained on the surfaces. The oxides are of different sizes, shapes and distributions. Also, the shape of the oxides and the surface covered by the oxides vary depending on the orientation of the steel grains.

The study of these surfaces allows to understand the influence of the oxide surface on wetting. However, a detailed wettability study of these surfaces is particularly complex given the anisotropy of the surface and the non-uniformity of the oxides. This would be easier by using model surfaces with controlled oxide shape and distribution.

These so-called patterned surfaces are widely used in the literature for wettability studies. Most of the surfaces are hydrophobic or super-hydrophobic (not wet by water). They are thus studied for their ability to repel water. In addition, they are also homogeneous, i.e. composed of a single chemical element.

Few wettability studies are devoted to heterogeneous patterned surfaces: substrate-defects by liquid metals at high temperatures. This is due to experimental difficulties and the difficulty of designing these heterogeneous surface types.

One of the design techniques for heterogeneous patterned surfaces is plasma enhanced chemical vapour deposition (PECVD) followed by a photolithographic process.

This technique was used to create patterned surfaces of Fe/silica with defects composed of amorphous silicon dioxide (SiO₂), whose lateral dimensions vary from $5 \times 5 \ \mu\text{m}^2$ to $500 \times 500 \ \mu\text{m}^2$ and the distances between defects vary from 5 μ m to 500 μ m [3].

The patterned surfaces reproduce well the type and chemistry of the silicon oxide layer formed during recrystallization annealing process: stoichiometric film and amorphous silicon dioxide. In this work, these surfaces are used for a detailed study of the wettability: influence of the size of the oxides, the distribution of oxides, the direction of spreading and the surface of the oxides.

Furthermore, the galvanization of steel sheets is carried out in a zinc alloy bath. The involved wetting is reactive. It leads to the formation of intermetallic compounds at the iron-zinc interface. These reactions modify the solid-liquid interface and add an additional complexity to the spreading dynamics of the zinc layer on the steel sheet. For these reasons, we do not provide, in this work, experiments with liquid zinc alloys. We were interested in a non-reactive liquid metal: lead. This allowed us to focus our study on the physical (non-reactive) wetting of textured iron-oxide surfaces by liquid metals.

Thus, this thesis work is divided into four parts or chapters.

The first chapter is devoted to the literature review. We will present the fundamental laws of capillarity and wetting. We will review some theoretical and experimental studies on the wetting of rough or heterogeneous surfaces. Then we will briefly present some general models

of wetting phenomena: contact angle, contact angle hysteresis and wetting transition (presence of gas under the drop or not). Concerning homogeneous and hydrophobic textured surfaces, we analysed about ten experiments published in the literature. We end with a summary of the rare experiments on heterogeneous textured surfaces at low and high temperatures.

The second chapter is devoted to the experimental devices and methods for characterizing the experimental tests performed. First, we will present the materials used: iron-silica patterned surfaces and lead metal. Then, the device of the dispensed drop technique. This device allows wettability tests to be carried out in a reducing environment composed of nitrogen (N2) and 5 vol. % of hydrogen. The fall of the drop and the spreading dynamics are then recorded using a high-resolution and high-speed camera. The images obtained are then processed by image processing methods, in order to reduce the time required for the treatment.

We will present the implemented automated procedures using MATLAB software.

The third chapter will discuss the main experimental results obtained by the dispensed drop technique. For that, we will first present the results obtained on pure substrates: pure iron and pure silica. The obtained results are considered as a reference for the study of textured surfaces. Then, the results of textured surfaces will be divided into several parts. First we will present the spreading dynamics of lead drop on surfaces of different pattern sizes and surface fractions. Then, we will focus on the phenomena of stick-slip motion often observed on surfaces with low silica coverage. The influence of this phenomenon will be studied at two different levels: during the spreading of the drop and on the solidified drop.

Afterwards, given the square shape of the oxides, the influence of the spreading direction of the drop will be studied, but also the shape of the solidified drop on the textured surfaces.

We will then discuss the influence of the size and distribution of silica patterns on wetting.

We will end this chapter by studying the influence of the oxide surface on wetting.

The last chapter will be concerned on the modelling of the observed different phases of the spreading dynamics. Given the complexity of the involved phenomena: rapid spreading dynamics, limitation of existing models. We will limit ourselves to the spreading diameter of the drop and its height and the involved oscillation of the drop.

In a first step, the drop advances and its spreading diameter increases. We will compare the evolution of the drop contact diameter during this phase with the classical laws of literature. At

the end of the first spreading, the drop is blocked for a few milliseconds at its maximum spreading diameter. We will see that this maximum diameter is a function of the impact velocity of the drop but also of the surface wettability. Then, the drop will recede and will oscillate before to stabilize. We will try to model the two observed oscillations of the drop: oscillation with mobile or fixed diameter. Furthermore, on surfaces with low silica coverage rates, the drop often splits when receding due to the stick-slip motion, we will try to explain this phenomenon from an energy point of view.

This work will end with a synthesis of the main results obtained and we will propose some suggestions which could help to answer some questions raised by this work.

I Literature review

I.1 General view on wetting and capillarity [4], [5]

I.1.1 Surface or interfacial tension

Inside a liquid phase, molecules are surrounded by other molecules and are subjected to cohesive interaction forces. At the interface with another medium (e.g., a vapour V), the interface molecules lose half of their neighbouring molecules, i.e. half of its cohesive interactions. The increase dA of the surface of the liquid L in contact with a vapour V thus requires δW work so that:

$$\delta W = \gamma_{LV} \,.\, dA \tag{I.1.1}$$

The surface (or interfacial) tension γ_{LV} of liquid *L* in contact with vapour *V* is then defined as the work per unit area (in mJ.m⁻²) required to increase the liquid surface.

If the cohesion energy per molecule is *E* inside the liquid, the energy lost by a molecule located at the surface is about *E*/2. Then, the order of magnitude of the surface tension γ_{LV} is:

$$\gamma_{LV} \approx \frac{E}{2 \cdot d_m^2} \tag{I.1.2}$$

with d_m a molecule characteristic dimension. γ_{LV} is expressed in J.m⁻² or N.m⁻¹.

For typical liquids, the cohesion energy *E* ranges from $k_B T$ (for Van der Waals interactions) to 100 $k_B T$ (for metallic bonds), leading to γ_{LV} from 20 mJ m⁻² (oils) and 72 mJ.m⁻² (water at 20°C) to a few hundred mJ.m⁻² (liquid metals) [5].

The surface tension can also be defined as the increase in Helmholtz free energy F_H due to the increase in the surface area, at constant volume V_L , temperature *T* and number of molecules *N*.

$$\gamma_{LV} = \left(\frac{\partial F_H}{\partial A}\right)_{T, V_L, N} \tag{I.1.3}$$

Surface energies are defined in the same way for solid / vapour and solid / liquid interfaces. They are called interfacial tensions and noted γ_{SV} and γ_{SL} respectively.

I.1.2 Surface curvature and pressure difference: Young-Laplace law

The shape of a liquid surface corresponds to the smallest possible surface area (Eq. (I.1.1)), due to the minimization of energy. For this reason, small drops and gas bubbles are almost spherical. In fluid dynamics calculations, the liquid surfaces taken into account are generally large enough

to be considered perfectly flat (e.g., in a tank). In this case, if the liquid is stagnant and in mechanical equilibrium, the pressure is the same on both sides of its surface.

The Young-Laplace law describes the case of the curved liquid surface. In fact, in the early nineteenth century, Thomas Young and Pierre-Simon Laplace discovered that there is a discontinuity in pressure through a non-planar interface.

Let us consider the curved surface element $d\vec{S}$ of a liquid as shown in Notations used for the Young-Laplace law on a curved surface [6]. in Figure I.1-1 [3]. This surface element is described by its two principal curvature radii R_1 and R_2 and its surface tension γ_{LV} . The pressure inside and outside the liquid is P_{in} and P_{out} respectively. At equilibrium, the resultant forces acting on the surface element, i.e. the pressure forces and the surface forces acting on its sides, are zero. The tangential component of the force balance includes only the surface forces. Then, the normal component of the force balance is given by:

$$-\gamma_{LV}d\theta_1d\theta_2R_1 - \gamma_{LV}d\theta_2d\theta_1R_2 + (P_{in} - P_{out}) x d\theta_1R_1 x d\theta_2R_2 = 0$$
(I.1.4)

The pressure difference across the surface can then be written as:

$$P_{in} - P_{out} = \gamma_{LV} \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \tag{I.1.5}$$

It is the Young-Laplace law. For a spherical interface, the two principal curvature radii are the same, i.e. $R_1 = R_2 = R$ and the pressure difference across the surface is given by Laplace's Law:

$$P_{in} - P_{out} = \frac{2\gamma_{LV}}{R} \tag{I.1.6}$$


Figure I.1-1. Notations used for the Young-Laplace law on a curved surface [6].

I.1.3 Capillary length [7]

As is commonly observed, the shape of a drop depends on its size. The small drops are spherical, while the larger ones are flattened by the effect of gravity. A characteristic length, called capillary length κ^{-1} , can be estimated by comparing Laplace pressure $\frac{\gamma_{LV}}{\kappa^{-1}}$ and hydrostatic pressure $\rho g \kappa^{-1}$ (at the depth κ^{-1} in the liquid, with ρ the liquid density and g the acceleration of gravity):

$$\kappa^{-1} = \sqrt{\frac{\gamma_{LV}}{\rho g}} \tag{I.1.7}$$

The effect of gravity can thus be neglected when the drop size is less than the capillary length. The capillary length is of the order of a few mm for most systems.

I.1.4 Contact angle of a liquid on a solid surface

Wetting refers to the study of the spreading of a liquid deposited on a solid (or liquid) substrate. As a result of Eq. (I.1.1), a small droplet placed on a solid surface takes the shape of a spherical cap in order to minimize system energy. The rim of the droplet where the three phases (solid, liquid and vapour) are in contact is called the triple contact line (*TCL*). And the wetting or contact angle θ is defined by the tangent to the droplet at the triple contact line.

The surface energies involved in wetting problems, can be compared by introducing the wetting parameter S_w .

$$S_w = \gamma_{SV} - \gamma_{SL} - \gamma_{LV} \tag{I.1.8}$$

Depending on the value of the wetting parameter, different configurations are possible (Figure I.1-2). The liquid drop can spread completely over the solid surface and form a continuous layer if $S_w > 0$ (i.e. the surface energy of the solid alone is higher than the surface energy of the wetted solid). This configuration is called perfect or complete wetting (e.g., water on very clean glass [4]). In this case, the contact angle θ is close to zero (Figure I.1-2c). However, perfect wetting is not the most common case. In most cases, $S_w < 0$ and the drop forms at equilibrium a spherical cap resting on the solid substrate with a contact angle θ . The wetting is then called partial and, three cases are possible depending on the value of the contact angle:

- High partial wetting if $\theta < 90^{\circ}$, the surface is said to be wetted by the liquid (or hydrophilic for water) (Figure I.1-2b) (e.g., lead / pure iron system [1], [8]);
- Low partial wetting if θ > 90⁰, the surface is not wetted by the liquid (or hydrophobic for water) (Figure I.1-2a) (e.g. lead / silica [1], [8]);
- No wetting if $\theta = 180^\circ$, the substrate is said to be superhydrophobic for water like Setcreasea or lotus leafs [9].



Figure I.1-2. Different wetting cases: non-wetted surface a) wetted surface b) perfect or complete wetted surface c) and non-wetted surface [10].

I.1.5 Contact angle on ideal solid substrates

At equilibrium, the contact angle of a drop on an ideal surface (i.e. homogeneous and smooth) can be determined by calculating the variation in surface energy associated with an infinitesimal displacement dx of the contact line (Figure I.1-3). If the drop volume is supposed to be unchanged, then:

$$dF = (\gamma_{LS} - \gamma_{SV})dx + \gamma_{LV}\cos\theta \,dx \tag{I.1.9}$$

where dF is the variation of Helmholtz free energy per unit length of the triple line.

At equilibrium, dF is equal to zero. Thus, the contact angle obtained on an ideal surface, denoted by θ_Y , is called the Young contact angle and is given by [11]:

$$dF = 0 \rightarrow \cos \theta_Y = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}$$
(I.1.10)



Figure I.1-3. The TCL displacement on an ideal surface modifies the surfaces of each interface (solid / liquid, solid / vapour and liquid / vapour)

We have therefore demonstrated that a droplet placed on an ideal surface forms a unique contact angle at equilibrium. This thermodynamic contact angle is the Young contact angle. However, most of the time, real surfaces cannot be considered as ideal, i.e. homogeneous and smooth. The following section will present the case of real surfaces.

I.1.6 <u>Contact angle on real solid substrates [4], [8]</u>

I.1.6.1. Contact angle hysteresis [4]

The determination of the thermodynamic contact angle requires very clean experimental conditions, i.e. homogeneous and smooth surface. In many practical situations, the triple line is pinned and immobile, not only for $\theta = \theta_Y$, but whenever θ lies within a finite interval around θ_Y :

$$\theta_r < \theta_Y < \theta_a \tag{I.1.11}$$

The advancing contact angle θ_a is measured when the solid / liquid contact surface increases, while the receding contact angle θ_r is measured when the solid / liquid contact surface shrinks (section I.1.6.2).

The contact angle hysteresis is defined as the difference between the advancing and receding contact angles. However, two definitions of the contact angle hysteresis ($\Delta\theta$ or *H*) are often used in the literature [4], [5], [8], [12]:

$$\Delta \theta = \theta_a - \theta_r \tag{I.1.12}$$

$$H = \frac{\theta_a - \theta_r}{\theta_a} \tag{I.1.13}$$

The value of contact angle hysteresis $\Delta \theta$ is commonly between 5 and 50° on real surfaces [13].

I.1.6.2. Measurements of advancing and receding contact angles

Contact angle hysteresis can be measured by means of a drop placed on a solid substrate (Figure I.1-4):

- The advancing contact angle θ_a is obtained when the drop volume is increased. The contact line remains pinned and the contact angle increases. The largest static contact angle, observed just before the *TCL* suddenly jumps, is the advancing contact angle.
- The receding contact angle θ_r is measured when the drop volume is decreased. The contact line remains pinned and the contact angle decreases. The smallest contact angle, below which the contact line recedes, is the receding contact angle.



Figure I.1-4. Contact angle hysteresis measurement a) advancing, b) receding contact angles [4].

Another way to measure the contact angle hysteresis is to place a drop on the initially horizontal substrate. The substrate is then tilted at a rate of approximately 0.1 to $0.7^{\circ}s^{-1}$ until the drop begins to slide [12]. By taking numerous images of the drop on the surface, the advancing and receding contact angles can be determined, as shown in Figure I.1-5, as the droplet begins to slide.



Figure I.1-5. Advancing and receding contact angles of a liquid drop on a tilted substrate [12].

Contact angle hysteresis can also be determined by the "sandwich drop" method. A liquid bridge, located between two parallel plates, is compressed and stretched successively very slowly. The two plates are identical and made of the solid substrate on which contact angles are studied [14], [15]. The advancing contact angle θ_a is measured during compression and the receding contact angle θ_r during stretching (Figure I.1-6). In this method, the equilibrium contact angle can also be obtained for the smooth homogeneous substrate during the spontaneous spreading of the drop on the surface.



Figure I.1-6. Principle of the sandwich drop method, the a) equilibrium, b) advancing, and c) receding contact angles are measured [14], [15].

The macroscopic contact angles (including the Young contact angle) are measured from the shadow images of the sessile drop or liquid bridge, in the plane perpendicular to the substrate and to the triple line.

The macroscopic contact angles also depend on how the drop spreads over the surface. The measured contact angle will depend on the metastable state in which the triple line is trapped. Thus, the correct interpretation of the contact angle measurement requires a careful characterization of the drop and the solid substrate, but also of how the triple line reached its position on the substrate [16].

I.1.6.3. Source of the contact angle hysteresis

A real solid surface is generally macroscopically rough (physical defects) and spotted with chemical heterogeneities (chemical defects). The triple line can be pinned to these defects, leading to multiple values for the observed contact angle.

The two examples described in Figure I.1-7 and Figure I.1-8 could explain the hysteresis mechanism. In the first example of a physical defect (Figure I.1-7), the triple line moves on a homogeneous solid and encounters a surface defect on which the opening angle is β . At point A, the apparent contact angle can take any value between θ_Y and $\theta_Y + (\pi - \beta)$ with θ_Y the intrinsic contact angle on the surface (or Young angle).



Figure I.1-7. Pinning of contact line on an angular defect [4], [8].

In the second example of a chemical defect (Figure I.1-8), the liquid recedes on a solid (from left to right) that contains a defect better wetted than the rest of the surface. The triple line thus moves to the right and meets the defect (Figure I.1-8a) which holds it, leading to the triple line corrugation (Figure I.1-8b). If the line still recedes, it will eventually detach from the defect (Figure I.1-8c).

Quantitatively, to detach the triple line from the defect, it is necessary to increase the force F_P (per unit length) applied to the triple line, i.e. to reduce the apparent angle θ^* . Thus, the triple line remains pinned by the defect for a certain range of angles below θ_Y .

$$F_P = \gamma_{LV}(\cos\theta^* - \cos\theta_V) \tag{I.1.14}$$



Figure I.1-8. Pinning of a contact line on a chemical defect [4].

These two examples show that on real surfaces, the observed static contact angle is not unique and can take any value within a certain range called contact angle hysteresis.

I.1.6.4. Effect of defect size

The effect of defect size on contact angles and contact angle hysteresis is not well known. Notwithstanding, it is important to note that the classical laws of contact angle are valid if the characteristic length of roughness or heterogeneity of the surface is much smaller than the size of the drop. In experiments, it is generally preferred to use drops smaller than the capillarity length ($\kappa^{-1} \approx 2.7 \text{ mm}$ for water at 25°C, i.e. with a drop volume less than 80 µl). The characteristic length of surface defects is in the order of a few tens of µm. The effect of defect sizes on tailored surfaces will be discussed deeply in chapter III.

For rough surfaces, the width of the hysteresis domain depends on the mean roughness value r_a (arithmetic average of the absolute values of the vertical deviations of the roughness profile from the mean plane) and the average wavelength λ_a of asperities ([9], [17]–[19]). According to experiments conducted by Hitchcock et al. [19], the effect of roughness on the contact angle is negligible when

$$\frac{r_a}{\lambda_a} < 10^{-3} \tag{I.1.15}$$

When the average surface roughness is low, contact angle hysteresis of only a few degrees can be expected and the Young contact angle can then be measured. For example, this was the case in the Hg / Al₂O₃ system when $r_a < 5 nm$ [20].

When the average surface roughness is high ($r_a > 1000 \text{ nm}$ [20]), the hysteresis domain is also reduced to a few degrees. In this case, a drop of non-wetting liquid cannot infiltrate into the surface cavities, resulting in the formation of a composite interface with air trapped under the liquid (see more details in section I.2.2).

With chemical heterogeneities, the triple line can be pinned to very small defects. μ m-sized heterogeneities were shown to pin the triple contact line at the macroscopic scale [21].

I.1.6.5. Shape of the triple line

Case of regular patterned homogeneous surfaces

Chatain et al. [14] studied the wetting of liquid lead on regular patterned silica surfaces with cylindrical pillars (Figure I.1-9). Due to heterogeneity, the triple contact line is distorted. The TCL preferably extends to areas where the contact angle is the lowest, here the top of the pillars,

as has been obtained in other experiments [22]. This phenomenon causes a TCL deformation which is different when the drop advances or recedes on the substrate. When air is trapped under the drop, the TCL appears to be strongly pinned when receding while the deformation is low when the TCL advances [14], [15], [22], [23].



Figure I.1-9. Triple line position of a liquid lead droplet on pillar-textured surfaces [14].

Case of regular patterned heterogeneous surfaces

The macroscopic contact angle of a drop deposited on a heterogeneous surface depends strongly on the location of the triple contact line. Here again, the triple line is affected differently when it advances or recedes: the receding *TCL* is pinned by the more wetting defects while the advancing *TCL* is pinned by the less wetting defects [14], [24]–[31]. As on homogeneous patterned surfaces, the triple contact line can be pinned on micron-sized defects, for example as shown in Figure I.1-10 for the wetting of silicon / silica substrates by liquid lead. Silicon is wetted by liquid lead whereas silica is not. The triple contact line remains pinned on the silicon squares leading to the *TCL* deformation [16].



Figure I.1-10. Triple contact line (TCL) of a tin droplet pinned on silicon squares organized on a silica surface. The inset shows a lower magnification micrograph where the silicon squares are white, the silica surface is dark, and the edge of the drop with its wandering triple line is light grey [16].

I.2 Models proposed for the wetting of non-ideal surfaces

I.2.1 Equilibrium contact angle

I.2.1.1. Wenzel and Cassie equations

As mentioned above, the Young's equation is only valid for a smooth and chemically homogeneous surface. Wenzel [32] in 1936 and Cassie [33] in 1944 were among the first to be interested in the equilibrium contact angle obtained on rough and heterogeneous surfaces (Figure I.2-1), respectively.



Figure I.2-1. A droplet on a) a rough surface and b) a composite surface.

Wenzel's law

On a randomly rough substrate, the local contact angle corresponds to the Young contact angle obtained on the smooth solid substrate. While the apparent contact angle at the macroscopic scale θ_W is given by Wenzel's law.

Let us consider an infinitesimal displacement dx of the triple contact line on the homogeneous rough surface of Figure I.2-1a. The variation of the Helmholtz free energy dF per unit length associated with this infinitesimal displacement is given by:

$$dF = (\gamma_{SL} - \gamma_{SV})r_W dx + \gamma_{LV} \cos \theta_W dx$$
(I.2.1)

with r_W the surface roughness, also called Wenzel's roughness. It is defined by the ratio between the actual surface area and its apparent value obtained in the horizontal plane ($r_W \ge 1$).

At equilibrium (dF = 0) and taking into account Young's equation (Eq.(I.1.10)), the macroscopic contact angle θ_w is given by Wenzel's law:

$$\cos\theta_W = r_W \times \cos\theta_Y \tag{I.2.2}$$

This energy minimization is valid for drops much larger than the characteristic length scale of the solid texture [7].

As Wenzel's law shows, a liquid will tend to spread more on a rough hydrophilic substrate. Conversely, a rough hydrophobic material appears more hydrophobic.

Cassie's law

Let us consider the case of a smooth and randomly heterogeneous surface, as shown in Figure I.2-1b, consisting of two different solids 1 and 2, with Young contact angles θ_{Y1} and θ_{Y2} and surface area fractions f_1 and $f_2 = 1 - f_1$. An infinitesimal displacement dx of the triple contact line on the surface causes a change in the Helmholtz free energy dF per unit length of the triple contact line:

$$dF = (\gamma_{SL1} - \gamma_{SV1}) f_1 dx + (\gamma_{SL2} - \gamma_{SV2}) f_2 dx + \gamma_{LV} \cos \theta_C dx \qquad (I.2.3)$$

where γ_{SLi} and γ_{SVi} are the surface energies for the solid/liquid and solid/vapour interfaces of solid *i* (*i* = 1 or 2).

At equilibrium, the apparent contact angle is given by Cassie's relation:

$$\cos\theta_C = f_1 \cos\theta_{Y1} + f_2 \cos\theta_{Y2} \tag{I.2.4}$$

For a heterogeneous surface composed of several different solids, the equilibrium contact angle is given by the generalized Cassie equation [14][33] [34]:

$$\cos\theta_C = \sum_i f_i \cos\theta_{Yi} \tag{I.2.5}$$

with $\sum_i f_i = 1$, f_i the surface area fraction and θ_{Yi} the Young contact angle of the ith solid.

I.2.1.2. Other laws using linear or surface fractions at the triple line

Different modified Cassie equations were proposed in order to take into account the interactions of the liquid and the solid at the triple contact line only [21] [35][36].

For a two-phase heterogeneous surface, the apparent contact angle can be expressed using the Young contact angles on the two solids (θ_{Y_1} and θ_{Y_2}) and the mean values of the line fractions of solid 1 and 2 along the triple contact line (λ_1 and λ_2) [21] [35][36].

$$\cos\theta^* = \lambda_1 \cos\theta_{Y1} + \lambda_2 \cos\theta_{Y2}$$
(I.2.6)
with $\lambda_1 + \lambda_2 = 1$.

The same equations were also proposed with the local surface area fractions of solid 1 and 2 near the triple contact line [37][38][39].

For heterogeneous surfaces composed of more than two solids, a generalized modified Cassie equation can also be found involving the linear fractions λ_i of the different solids *i* at the triple contact line:

$$\cos\theta^* = \sum_i \lambda_i \cos\theta_{Yi} \tag{I.2.7}$$

with $\sum_i \lambda_i = 1$.

I.2.1.3. Discussion on the validity of Wenzel and Cassie's law

Of course, the contact angle at equilibrium is determined by the interactions of liquid and solid at the triple contact line. If the solid surface at the triple contact line is different from the solid surface under the liquid drop, the apparent contact angle cannot be calculated by Wenzel or Cassie's laws, which take into account the surface area under the liquid drop (see for example the experiments from [40], [41]). Pease [36] was one of the first in 1945 to suggest that the contact angles on a surface are given only by interactions at the triple contact line. After this work, many other authors proposed that the contact angles and the shape of the drop are determined solely by the TCL and are not altered by surface irregularities under the drop [18], [19], [35], [38]–[45].

At the same time, other surface scientists have suggested that the classical Cassie and Wenzel laws are valid if the drop is large enough compared with the wavelength of roughness or chemical heterogeneity [37], [39], [47]–[52]. Roughness and heterogeneity parameters should be uniformly constant and should not depend on droplet location or droplet contact surface size. Then, the deviation of the measured contact angles from the Cassie and Wenzel predictions may be explained by uncertainties in the measurements related to various experimental techniques and distortions of actual contact lines.

Currently, it is clear that the contact angle and hysteresis are governed by the events that occur at *TCL*. It is generally expected that the Young equation is locally valid and that the macroscopic contact angle is determined by the shape of the contact line. However, most of the time, experimental conditions are chosen to be in the case of the validity of Wenzel and Cassie's laws

because the contact area fraction can be easily evaluated while the actual form of the *TCL* is very difficult to know.

I.2.2 Wetting transition

Two different wetting regimes are possible when a liquid drop is deposited on a rough and homogeneous solid. In fact, if the solid substrate is not well wetted by the liquid (Young contact angle higher than 90°): the liquid drop can completely fill the texture (Wenzel regime) or sit on a composite surface composed of solid and air (Cassie regime) (Figure I.2-2).



Figure I.2-2. Liquid deposited on a model surface with spikes: for contact angles larger than 90°, the liquid drop can completely fill the texture (left) or air can be trapped below the liquid, inducing a composite interface between the solid and the drop (right).

Even if there is a hot debate [53] on the role of the triple line or the contact surface of the drop on the apparent angle (section I.2.1.3), it is widely admitted that the wetting regime is characterized by the physical and chemical properties of whole surface under the droplet [4], [5], [54].

We are interested here in the transition from the Wenzel regime to the Cassie regime in the case of low partial wetting (Young contact angle higher than 90°).

Wenzel regime

In the case of the Wenzel regime, the apparent contact angle at equilibrium is given by Wenzel's law (Eq. (I.2.2)).

Cassie regime

When the Young contact angle is larger than 90°, the liquid drop deposited on the solid with a very high surface roughness cannot follow all the irregularities of the solid ($\gamma_{SV} < \gamma_{SL}$). Air can remain trapped inside the texture and the liquid drop rests on a composite surface composed of

solid and air [33]. In this case, the apparent contact angle θ^* at equilibrium is given by Cassie's equation with $\theta_{Yair} = 180^\circ$ (the shape of a small liquid drop in air is spherical, corresponding to a contact angle of 180°).

$$\cos\theta^* = f_S \cos\theta_{YS} - 1 + f_S \tag{I.2.8}$$

where f_S is the surface area fraction of the solid in direct contact with the liquid and θ_{YS} is the Young contact angle of the liquid on the solid.

The air/liquid interfaces under the liquid drop are nearly flat as their curvature is the same as the drop of larger size than the size of the asperities [4],[7].

Cassie to Wenzel transition: classical law [4], [8], [34].

To find the condition for air entrapment under the liquid drop, the change in Helmholtz free energy associated with an infinitesimal displacement dx of the triple contact line on the surface is estimated in the Wenzel regime (Figure I.2-2 left) and in the Cassie regime (Figure I.2-2 right). The Cassie state is selected when:

$$(\gamma_{SL} - \gamma_{SV})f_S dx + \gamma_{LV}(1 - f_S)dx < (\gamma_{SL} - \gamma_{SV})r_W dx$$
(I.2.9)
i.e., knowing that $\gamma_{SL} - \gamma_{SV} = -\gamma_{LV} cos \theta_Y$ (Eq. (I.1.10)),

$$\theta_Y > \theta_{crit} > 90^\circ \text{ with } \cos\theta_{crit} = \frac{f_S - 1}{r_W - f_S}$$
(I.2.10)

In Figure I.2-3, $cos\theta^*$ is plotted as a function of $cos\theta_Y$ in the case of Wenzel state ($\theta_Y < \theta_{crit}$) and in the case of Cassie state ($\theta_Y > \theta_{crit}$, Eq. (I.2.10)).



Figure I.2-3. Possible configurations of a droplet on a surface as a function of Young contact angle (higher than 90°), a) the drop rests on a composite surface with air trapped under the droplet, b) the texture is filled with liquid under the droplet [9].

In our work, the studied solid samples are made of iron covered with square-based and regularly spaced silica pillars. For this reason, the following discussion will be restricted to the tailored surface configuration. Let us consider the case of a crenelated substrate in contact with a liquid drop, exhibiting a low partial wetting (Young contact angle higher than 90°). Both Wenzel and Cassie states are possible (Figure I.2-2).

If one considers a homogeneous textured surface composed of square-based pillars in a square distribution (Figure I.2-4), then:

$$f_{S} = \frac{1}{\left(1 + \frac{s}{d}\right)^{2}} \text{ and } r_{W} = 1 + \frac{4 * \frac{h}{d}}{\left(1 + \frac{s}{d}\right)^{2}}$$
(I.2.11)

The geometrical parameters are *d* the side length of the square pillars, *h* their height and *s* the distance between them. In the plane $\left(\frac{s}{d}, \frac{h}{d}\right)$, the transition from the Cassie regime to the Wenzel regime (*C*-*W*) is calculated from Eq. (I.2.9) and occurs when:

$$\left(\frac{s}{d}\right)_{C-W} > \left[1 - 4\left(\frac{h}{d}\right)\frac{\cos\theta_Y}{1 + \cos\theta_Y}\right]^{1/2} - 1 \tag{I.2.12}$$

Chapter I: Literature review



Figure I.2-4: Definitions of parameters for a textured square pillars in a square arrangement [35].

Although the Cassie state is often observed even if the condition given by Eq. (I.2.12) is not fulfilled (see section I.3.4), in experimental studies using water drops gently deposited on textured surfaces. This means that the Cassie state might be metastable, i.e. it might exist instead of the stable Wenzel state. The metastable Cassie state is represented in Figure I.2-3 by the dotted black line. In the case of a crenelated solid, the existence of air/liquid interfaces below the drop might be due to the pinning of the triple line on the sharp edges of the surface [7].

Many models have been proposed to more accurately predict this wetting transition (see for example [55], [56], [57], [60]). Since only one regime (the Wenzel regime) was observed in our experiments, these models are detailed only in appendix C of this report.

I.2.3 Contact angle hysteresis

On real surfaces, the equilibrium contact angle is not easy to measure because the static contact angle can take all the values in the hysteresis range. It is therefore more relevant to determine the contact angle hysteresis, which is more characteristic of droplet wetting on non-ideal surfaces.

Many models have been developed to predict the contact angle hysteresis of a liquid drop advancing or receding on rough or heterogeneous substrate.

A first family of models is based on free energy thermodynamic analysis (see for example [17], [59]-[60]). The total Helmholtz free energy of the system can be estimated by the sum of three terms, corresponding to the energy of each interface multiplied by its area. The evolution of Helmholtz free energy as a function of the macroscopic contact angle θ of the drop is a succession of local minima and local maxima (sawtooth curve). The absolute minimum of the curve corresponds to the stable Wenzel or Cassie contact angle. The local minima (resp.

maxima) correspond to the metastable (resp. unstable) positions of the triple line on the substrate. The difference between two successive minimum and maximum is the energy barrier to overcome when the drop advances or recedes. With such an approach, the prediction of the contact angle hysteresis needs the value of these energy barriers, which are not very well-known at present [59], [60], [61].

A second family of models attempts to link the contact angle hysteresis to the distortion of the contact line on the heterogeneities of the substrate. For pinning defects far apart from each other, the contact angle hysteresis is generally evaluated using the approach proposed by Joanny and de Gennes [62]. For the advancing contact angle, this approach leads to the following equation [4], [62], [63]:

$\gamma(\cos\theta_E - \cos\theta_a) = n_d E_{diss} \tag{I.2.13}$

where θ_E is the equilibrium contact angle on the hererogeneous or rough substrate, n_d is the number of defects per unit area and E_{diss} is the dissipated energy for a single pinning defect as the triple line advances. E_{diss} is related to the shape of the triple line among other physical and geometrical parameters.

A third and final family of models combines the two approaches, namely thermodynamic analysis and the contribution of the triple line. Among the proposed models [64], [65], we will detail the one we have chosen to compare with our results because the demonstration presented in the publication is the most complete [65]. The equations are established in the case of a substrate (subscript 2) covered by discrete defects (subscript 1). Defects 1 are better wetted by the liquid than substrate 2, i.e. $\theta_{Y1} < \theta_{Y2}$. A droplet whose volume decreases and which consequently recedes is considered. In this case, the volume loss is compensated either by a decrease in the contact angle when the contact line remains pinned (pinning mode, subscript *P*) or by the receding of the triple line with a constant receding contact angle (receding angle mode, subscript *R*).

In the first step of the demonstration, the behaviour of a model droplet without contact line distortion is studied. If the contact line is pinned, the variation in the Gibbs free energy of the system due to volume loss depends only on the variation of the liquid/vapour surface and is given by:

$$dG_P = 2\pi R^2 \gamma_{LV} \frac{1 - 2\cos\theta + \cos^2\theta}{\sin\theta} d\theta \tag{I.2.14}$$

where θ is the instantaneous contact angle that the droplet makes with the surface and *R* is the radius of curvature of the droplet, assumed to be in the shape of a spherical cap.

If the contact line recedes, the variation in the Gibbs free energy of the system due to volume loss involves a solid-liquid area change and is given by:

$$dG_R = 2\pi R \gamma_{LV} (-\sin^2 \theta . \cos \theta_C + 2(1 - \cos \theta)) dR$$
(I.2.15)

where θ_c is the Cassie contact angle given by Eq. (I.2.4).

Finally, the pinning mode and the constant receding angle mode can be compared using the ratio between the Gibbs free energy variations described above:

$$\frac{dG_P}{dG_R} = \frac{2 - 3\cos\theta + \cos^3\theta}{-\sin^2\theta \cdot \cos\theta_C + 2(1 - \cos\theta)}$$
(I.2.16)

For a receding droplet, when $\theta > \theta_C$, $dG_P < dG_R < 0$ and the pinning mode is thermodynamically favoured. The instantaneous contact angle continues to decrease until it reaches θ_C at which $dG_P = dG_R$. The constant receding angle mode is then thermodynamically favoured, resulting in the contact line depinning. In this analysis, the receding contact angle is given by the Cassie contact angle because the distortion of the triple line is not taken into account.

In the second step of the demonstration, the contact line is considered to be tortuous because it is distorted along the more hydrophilic defects. The energy ratio defined in Eq. (I.2.16) becomes:

$$\frac{dG_P}{dG_R} = \frac{2 - 3\cos\theta + \cos^3\theta}{-\sin^2\theta(\lambda_1\cos\theta_{Y1} + (1 - \lambda_1)\cos\theta_{Y2}) + 2(1 - \cos\theta)}$$
(I.2.17)

where λ_1 is the contact line fraction on the defects.

The droplet will be pinned during its receding until the maximum possible deformation of the triple line is reached. At this point, the contact line fraction on the defects is noted λ_{1max} and $dG_P = dG_R$ with $\theta = \theta_r$ leading to:

$$\cos \theta_r = \lambda_{1max} \cos \theta_{Y1} + (1 - \lambda_{1max}) \cos \theta_{Y2}$$
(I.2.18)

The same reasoning can be done for an advancing contact line.

 $\cos \theta_a = \lambda_{2max} \cos \theta_{Y2} + (1 - \lambda_{2max}) \cos \theta_{Y1}$ (I.2.19)

Until now, substrate 2 and defects 1 were assumed to be perfectly smooth. In the third step of the demonstration, they are expected to display an intrinsic contact angle hysteresis. In this case, the last two relationships can be rewritten as:

$$\cos \theta_r = \lambda_{1max} \cos \theta_{r1} + (1 - \lambda_{1max}) \cos \theta_{r2}$$
(I.2.20)

$$\cos \theta_a = \lambda_{2max} \cos \theta_{a2} + (1 - \lambda_{2max}) \cos \theta_{a1}$$
(I.2.21)

where θ_{r1} (resp. θ_{r2}) and θ_{a1} (resp. θ_{a2}) are the receding and advancing contact angles on the surface of defect 1 (resp. substrate 2).

This model [65] will be compared to our experimental results in section III.7.2.

The aim of this work is to study the wetting of heterogeneous iron/silica substrates with liquid lead. The silica, in the form of square prisms, will be distributed regularly in a square arrangement on iron. Iron is wetted by liquid lead while silica is not. For this reason, the literature review presented here is limited to the wetting of solid substrates with regular patterns by liquids. At first, we will focus in section I.3 on textured homogeneous solids with low partial wetting to understand the influence of defect network. Then, section I.4 will be devoted to heterogeneous textured substrates.

I.3 Wetting of textured homogeneous surfaces

I.3.1 Geometry of the solid substrates considered

We will focus on the results obtained for six types of homogeneous patterned solid substrates, with different shapes and distributions of the pillars (Table I.3-1 and Table I.3-2). The selected surfaces are composed of square or cylindrical pillars in a square or hexagonal distribution. The hexagonal distribution can be regular or irregular (made of isosceles triangles). The patterned solid surfaces will be denoted as SS, SH_{reg} , SH_{irreg} for square pillars in a square, regular hexagonal and irregular hexagonal arrangement respectively and CS, CH_{reg} , CH_{irreg} for cylindrical pillars in a square, regular hexagonal and irregular sin a square, regular hexagonal and irregular sin a square, regular hexagonal and irregular hexagonal arrangement respectively. The geometrical parameters are *d* the side length of the square pillars or the diameter of the cylindrical pillars, *h* their height and *s* the distance between them.

Table I.3-1: Different texture	es with square	pillars and	corresponding	surface]	parameters
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Texture	Cassie fraction	Wenzel roughness	Geometrical factor	Refs.
$ \begin{array}{c} SS^{(a)} \\ \downarrow S \\ \downarrow S \\ \end{array} $	$f = \frac{1}{\left(1 + \frac{s}{d}\right)^2}$	$r_w = 1 + \frac{4 \times \frac{h}{d}}{\left(1 + \frac{s}{d}\right)^2}$	$G_f = 1$ $d_{eq} = d$	[66]–[73]
$SH_{reg}^{(b)}$	$f = \frac{2}{\sqrt{3}} \frac{1}{\left(1 + \frac{s}{d}\right)^2}$	$r_w = 1 + \frac{8}{\sqrt{3}} \frac{\frac{h}{d}}{\left(1 + \frac{s}{d}\right)^2}$	$G_f = \frac{2}{\sqrt{3}}$ $d_{eq} = d$	[74]
SH _{irreg} ^(c)	$f = \frac{1}{\left(1 + \frac{s}{d}\right)^2}$	$r_w = 1 + \frac{4 \times \frac{h}{d}}{\left(1 + \frac{s}{d}\right)^2}$	$G_f = 1$ $d_{eq} = d$	[23]

(a) SS: square pillars, square arrangement; (b) SHreg: square pillars, regular hexagonal arrangement; (c) SHirreg: square pillars, irregular hexagonal arrangement.

Table I.3-2: Different textures with cylindrical pillars and corresponding surface parameters.

Texture	Cassie fraction	Wenzel roughness	Geometrical factor	Refs.
$CS^{(a)}$	$f = \frac{\pi/4}{\left(1 + \frac{s}{d}\right)^2}$	$r_w = 1 + \frac{\pi \times \frac{h}{d}}{\left(1 + \frac{s}{d}\right)^2}$	$G_f = \frac{\pi}{4}$ $d_{eq} = \frac{\sqrt{\pi}}{2}d$	[55], [56], [73], [75], [76]
CH _{reg} ^(b)	$f = \frac{\pi}{2\sqrt{3}} \frac{1}{\left(1 + \frac{s}{d}\right)^2}$	$r_w = 1 + \frac{2\pi}{\sqrt{3}} \frac{\frac{h}{d}}{\left(1 + \frac{s}{d}\right)^2}$	$G_f = \frac{\pi}{2\sqrt{3}}$	[15], [71], [77]



(a) CS: cylindrical pillars, square arrangement; (b) CHreg: cylindrical pillars, regular hexagonal arrangement; (c) CHirreg: cylindrical pillars, irregular hexagonal arrangement.

For these textured surfaces, the Wenzel roughness r_W and the surface area fraction of the pillar tops f_S (section I.2.1.1) can be calculated as follows:

$$r_W = 1 + \frac{4 \times G_f \times \frac{h}{d}}{\left(1 + \frac{s}{d}\right)^2}, \qquad f_S = \frac{G_f}{\left(1 + \frac{s}{d}\right)^2}$$
(I.3.1)

where G_f is a geometrical factor characteristic of pillar shapes (Table I.3-1 and Table I.3-2).

If one considers a dimensionless analysis, the apparent contact angle θ^* of a drop deposited on a solid surface depends on three groups of variables:

- Surface wettability: interfacial energies involved in the system $(\gamma_{LV}, \gamma_{SV}, \gamma_{SL})$ or the associated Young's angle and the interfacial energy of the liquid phase (γ_{LV}) .
- Hydrostatic parameters: drop density (ρ), gravity acceleration (g) and drop size (R).
- Surface geometry: *h*, *d*, *s*.

The systems considered here can therefore be described by nine physical variables, two of which are non-dimensional (θ^*, θ_{YS}) , the other seven are expressed by three physical dimensions (kg, m, s). From the Buckingham π theorem, it can be deduced that the system under consideration can be described by six non-dimensional numbers, namely θ^* , θ_{YS} , $\frac{h}{d}, \frac{s}{d}, \frac{R}{s}, \frac{Rd}{k^{-2}}$ (appendix A).

The liquid drops considered in the literature review are much larger than the texture dimensions. The influence of $\frac{R}{s}$ can therefore be neglected. The influence of the hydrostatic pressure of the drop compared to the wetting properties of the system, given by a criterion on the dimensionless number $\frac{Rd}{\kappa^{-2}}$ (in the order of 10⁻⁴, for a millimetre drop) can also be neglected. Finally, only two dimensionless lengths $\frac{h}{d}$, $\frac{s}{d}$ will be used to allow comparisons between the different experimental studies.

To compare the different geometries considered here, the regular arrangement with square pillars is chosen as the reference geometry. The other geometries are converted to this reference geometry using an equivalent side length (d_{eq}) , equivalent height (h_{eq}) and equivalent distance between them (s_{eq}) . These three geometrical parameters are calculated by keeping constant all surfaces in contact with the liquid, i.e., the surface area of the pillar tops, the lateral surface area of the pillars and the surface area of the elementary cell of the two-dimensional network. The equivalent side length is unchanged for square pillar and for a cylindrical pillar, it is given by:

$$\frac{\pi d^2}{4} = d_{eq}^2 \tag{I.3.2}$$

The equivalent distance between pillar and their height can be calculated from Eq. (I.3.1),

$$\frac{G_f}{\left(1+\frac{s}{d}\right)^2} = \frac{1}{\left(1+\frac{s_{eq}}{d_{eq}}\right)^2}, \qquad \frac{4 \times G_f \times \frac{h}{d}}{\left(1+\frac{s}{d}\right)^2} = \frac{4 \times \frac{h_{eq}}{d_{eq}}}{\left(1+\frac{s_{eq}}{d_{eq}}\right)^2}$$
(I.3.3)

Then, we obtain, after some manipulations:

$$\frac{s_{eq}}{d_{eq}} = \frac{1}{\sqrt{G_f}} \left(1 + \frac{s}{d} \right) - 1; \quad \frac{h_{eq}}{d_{eq}} = \frac{h}{d}$$
(I.3.4)

I.3.2 Wetting conditions

The main objective of our research work is to study the wetting of regular silica-patterned iron by liquid lead. In this system, the contact angle on silica is around 120° [1], [78]. In the review presented here, the wetting conditions were chosen to allow comparison with these experiments. The selected publications therefore focused on systems exhibiting a Young contact angle on the smooth surface of about $\theta_Y \sim 120^\circ$.

Many authors [15], [23], [56], [66]-[77] have studied the wetting of homogeneous textured surfaces at low temperatures, often to study their super-hydrophobicity. In the field of liquid metals, we found only two references [14], [15] on the physical wetting (without any chemical reactions between liquid and solid components) of homogeneous patterned surfaces. The

systems used (liquid and solid) and the Young contact angle are given in Table I.3-3 for each selected experiment and the corresponding pillar dimensions are presented in Table I.3-4.

Ref.	Liquid	Solid	Texture	Contact angle
1 [66]	Water (1µl)	Fluorosilane	SS	$\theta_Y = 114^{\circ}$
2 [67]	Water	FT silane	SS	$ heta_a = 120^\circ$, $ heta_r = 80^\circ$
3 [69]	Water	PFA polymer	SS	$ heta_a=120^\circ$, $ heta_r=71^\circ$
4 [70]	Water (4-10µ1)	PFO silane	SS	$\theta_Y = 115^{\circ}$
5 [71]	Water (6µl)	PFT silane	SS	$\theta_Y = 107^\circ$
6 [72]	Water (2-6µl)	OT silane	SS	$\theta_Y = 111.8^{\circ}$
8 [73]	Water (3.5-8.5 µl)	DMDC silane	SS, CS	$\theta_Y = 106^{\circ}$
7 [74]	Water (8ul)	OT silane	SS, SH_{reg}	$\theta_{\rm rr} = 107$
, [, ,]	() alor (0µ1)	01 shulle	CS, CH_{reg}	0y - 107
8 [23]	Water (5-15ul)	Silane agents	SHirmon	$\theta_a = 107 - 119^\circ$
0 [20]		Shane agents	trrey	$\theta_r = 94 - 110^\circ$
9 [55]	Water (2-10µl)	PDM silane	CS	$ heta_a=116^\circ$, $ heta_r=104^\circ$
10 [75]	Water (3-15µl)	PF ₃ silane	CS	$\theta_Y = 109^{\circ}$
11 [56]	Water (6µl)	PDM silane	CS	$\theta_Y = 110^{\circ}$
12 [77]	Water (25-75µl)	TPF silane	CH_{reg}	$\theta_a = 113^\circ$, $\theta_r = 91^\circ$
13 [14]	Lead (54 mm^3)	Silica	CH _{irreg}	$\theta_{YS} = 110^{\circ}$
14 [15]	$Tin (1 cm^3)$	Silica	CH _{reg}	$\theta_{Y,Silica} = 124 - 129^{\circ}$

Table I.3-3: Liquid / solid systems for each experiment from the literature presented in this work.

Table I.3-4: Pillar dimension	for each set	lected experiment.
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Ref. Textu	Toyture type	Pillar size	Pillar space	Pillar height
	Texture type	d (µm)	s (µm)	$h(\mu m)$
1 [66]	SS	50	100	10-282
2 [67]	SS	3-9	3-20	0.04-18.59
3 [69]	SS	8, 16, 32	4.17, 8, 16	40
4 [70]	SS	12, 18	18-48	30
5 [71]	SS	2.44-4.93	0.07-256	2

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('hontor	••	1 itoroturo	routout
LIADIEL			IEVIEW
Cinapter	••	Dittitutuit	10,10,0
-			

6 [72]	SS	9-85.8	5.74-31.61	16
8 [73]	SS, CS	8-100	8-50	30-34
7 [74]	SS, SH _{reg}	56-60		
, [, <u>,</u>]	CS, CH_{reg}	50-00	_	_
8 [23]	SH _{irreg}	2-126	2-128	20-140
9 [55]	CS	10	5-140	40
10 [75]	CS	5, 14	2-198	30
11 [56]	CS	5	5-50	5-25
12 [77]	CH_{reg}	20.9-42.3	2-92	30
13 [14]	CH _{irreg}	30	7, 13	3, 30
14 [15]	CH _{reg}	60	40, 130	0.00335

I.3.3 Measured contact angles

In this section, the evolution of the advancing (section I.3.3.1) and receding (section I.3.3.2) contact angles will be studied as a function of the two dimensionless lengths mentioned before $(\frac{s_{eq}}{d_{eq}}, \frac{h_{eq}}{d_{eq}})$, for the six types of textured surfaces shown in Table I.3-1 and Table I.3-2. The review is intentionally focused on publications that present measurements of advancing and receding contact angles. When a single contact angle is measured with the sessile drop technique, this contact angle is not necessarily the equilibrium contact angle, since the liquid drop can be pinned at any contact angle in the range of the contact angle hysteresis (section I.1.6). From these experimental points, the wetting transition from Wenzel state to Cassie state will be investigated (section I.3.4).

I.3.3.1. Advancing contact angle

For clarity, we will present here the results in the case of square pillars in a square distribution (SS). The evolution of the advancing contact angle as a function of $\frac{s_{eq}}{d_{eq}}$ (top) and $\frac{h_{eq}}{d_{eq}}$ (bottom) is shown in Figure I.3-1. Overall, the experimental points are consistent with each other. And that for all the data taken from different references [67], [69], [70], [73].

When s/d is increased, θ_a increases to a maximum of about 160° and then gradually decreases. This decrease begins at a larger s/d when h/d is increased (see for example h/d = 0.5 to 1.5, Figure I.3-1 top).

When h/d is increased, θ_a significantly increases and then remains stable at about 160°. The advancing contact angle increases more rapidly with h/d when s/d is lower (Figure I.3-1 bottom).

The evolution of the advancing contact angle can therefore be divided into two zones. The boundary between them depends on the values of s/d and h/d. At the highest values of s/d or the lowest values of h/d, i.e. the highest values of the spacing between pillars or the lowest values of their height, the liquid drop completely fills the hydrophobic texture and is in the Wenzel regime. In the other hand, at the lowest values of s/d or the highest values of h/d, the liquid drop rests on a composite surface composed of solid and air. This wetting state is called the Cassie regime.

The comparison between the experimental points and the Wenzel and Cassie's laws are detailed in appendix C.1 and to the models of contact angle hysteresis in appendix C.3.





Figure I.3-1. Advancing contact angle as a function of the dimensionless lengths s/d (top) and h/d (bottom) [67], [69], [70], [73].

I.3.3.2. Receding contact angle and contact angle hysteresis

Square pillars in a square distribution

The evolution of the receding contact angle (empty points) as a function of s/d (top) and h/d (bottom) is represented with the corresponding advancing contact angles (full points) in Figure I.3-2. The dispersion of the experimental points obtained for the receding contact angle is much larger than that of the advancing contact angle. This could be explained by a stick-slip movement of the triple line pinned by the top of the pillars when it recedes. This is not the case when it advances because the drop slips on the air entrapped in between the pillars [23], [59], [65].

As a general trend, the receding contact angles are smaller than the advancing contact angles and the contact angle hysteresis is larger in the Wenzel regime than in the Cassie one.

When h/d is increased from 0 to 7, i.e. Wenzel roughness is increased, θ_r decreases to a contact angle of about 60° and then discontinuously jumps to a value higher than 120° (Figure I.3-2 bottom). This evolution is in excellent agreement with the experiments of Johnson and Dettré

[79]¹ (Figure I.3-3). This example is often chosen to illustrate the concept of contact angle hysteresis [7], [59], [62], [80]–[82].

¹ Johnson and Dettré measured the advancing and receding contact angles of water on wax substrates. The surface roughness of the wax samples was reduced by means of successive heat treatments. The surface roughness is only qualitative in this paper.



Figure I.3-2. Advancing (full points) and receding (empty points) contact angles as a function of the dimensionless lengths s/d (top) and h/d (bottom) [67], [69], [70], [73].



Figure I.3-3: Advancing and receding contact angles of water on wax substrates, depending on the substrate roughness [79].

In the Wenzel regime, the advancing contact angle increases with surface roughness, which means that the hydrophobicity of the solid increases as predicted by Wenzel (Eq. (I.2.2)). At the same time, the receding contact angle is reduced and exhibits a surprising hydrophilic behaviour ($\theta_r < 90^\circ$) despite the hydrophobic nature of the smooth substrate. This is explained by Quéré [7]. As the contact line recedes, some of the liquid may remain trapped in the cavities of the solid surface, resulting in a significant decrease in the contact angle, as the drop is in contact with both the hydrophobic solid and the liquid at the triple line. In this condition, the greater the amount of liquid trapped in the texture, i.e. the higher the surface roughness, the smaller the receding contact angle.

Metastable Cassie state can also be observed in the range of stable Wenzel regime (see for example the receding contact angles of 120° when h/d is less than 1.0. The coexistence of the two regimes has already been demonstrated by Lafuma and Quéré [83] in the case of moderately

rough substrates and by Park et al. [56] for the wetting of micro-structured surfaces with hydrophobic and hydrophilic materials.

Other geometries: the influence of the shape and distribution of textures

Figure I.3-4 shows the influence of pattern shape (*SS* and *CS*) on the equilibrium (\bigcirc), advancing (\blacksquare) and receding (\square) contact angles. In this figure, the data are collected from different references [56], [66], [67], [71]–[73]. Despite the discrepancy of the data due to the differences in the used materials of each reference, the influence of pattern shape is not evident.

Moreover, the influence of pattern shape and distribution is not well-known. Yu et al [74] studied the influence of the four types of homogeneous textured surface (*SS*, *SH*_{reg}, *CS* and CH_{reg}). The contact angle hysteresis on all the four studied textures follow the same trends in agreement of the classical laws, Figure I.3-5. Also, the advancing contact angles are nearly constant where the receding contact angle decreases when the Cassie fraction increases.

The contact angle seems to be different from a texture to another, at a given area fraction of the patterns. This can be explained by the fact that the triple contact line is not affected in the same manner when advancing or receding from a texture type to another. McCarthy and Öner [23] suggested the *TCL* to be more pinned to the indented square pillars than to the staggered rhombus pillars and then the receding contact angle weaker.

In the case of textured surfaces with square and cylindrical pillars of our analysis (Figure I.3-5) any significant difference can be noticed. However, it seems that the advancing and receding contact angles depend on texture shape and distribution, but the difference is relatively small compared to the experimental errors (more than $\pm 5^{\circ}$).



Figure I.3-4: Influence of the shape and distribution of textures at given $(s/d)_{eq}$. Equilibrium (empty circle, O), advancing (full square, \blacksquare) and receding (empty square, \square) contact angles as a function of the equivalent dimensionless lengths s/d. SS surfaces are in square marks and CS in circle marks [56], [66], [67], [71]–[73].



Figure 1.3-5: Influence of patterns shape and distribution at given area fraction of pillars. Advancing contact angles are in full marks and receding contact angles in empty marks [74].

I.3.3.3. Equilibrium contact angle

In some references [55], [66], [71], [72], [75], a single contact angle, generally called equilibrium contact angle, is measured with the sessile drop technique. The evolution of these so-called equilibrium contact angles $\theta_E(*)$ as a function of s/d (top) and h/d (bottom) is shown in

Figure I.3-6: Equilibrium (*), advancing (\bullet) and receding (O) contact angles as a function of the dimensionless lengths s/d (top) and h/d (bottom) [55], [66], [67], [69]–[73], [75].

with the corresponding advancing (•) and receding (O) contact angles from other references [67], [69], [70], [73]. As expected, the equilibrium contact angles are located between the advancing and receding contact angles. Most of the time, the so-called equilibrium contact angle θ_E is of the same order of magnitude as the advancing contact angle, which could be explained by the technique used to measure it: In the sessile drop technique, the drop is deposited on the solid substrate and spreads on it.



Figure I.3-6: Equilibrium (*), advancing (\bullet) and receding (O) contact angles as a function of the dimensionless lengths s/d (top) and h/d (bottom) [55], [66], [67], [69]–[73], [75].

I.3.4 Wetting transition

The experimental results obtained for the advancing contact angle are divided into two zones, as in Figure I.3-1: Wenzel regime and Cassie regime. When h/d is increased, θ_a significantly increases (Wenzel regime) and then remains stable at about 160° (Cassie regime). The boundary between the two regimes corresponds to a pair {h/d; s/d} which can be derived from the curves in Figure I.3-1 for each set of experimental points. This was done for the references presented in Table I.3-3 at low temperature (water): [23], [55], [56], [73], [75], [77]. Figure I.3-7 shows all the experimental pairs recorded, corresponding to the liquid / solid (\blacksquare) (Wenzel state) or liquid / air / solid (\Box) (Cassie state) interfaces in a {h/d; s/d} plane.

The experimental transition from the Cassie state to the Wenzel state (dashed line in Figure I.3-7) is then deducted from the data of wetting by water. The experimental curve significantly deviates from the theoretical Wenzel/Cassie transition of Eq. (I.2.12) (full line in Figure I.3-7). Indeed, as explained in section I.2.2 Cassie state could be observed even if the thermodynamic condition is not fulfilled in the case of a drop gently deposited on textured surfaces: metastable Cassie state.

Further, the experimental transition suggests the existence of a minimum value of h/d (around 0.4) for the Cassie regime. Under this minimum value, the Cassie regime should not exist, as explained by Extrand [58]. In fact, while suspended on textured surfaces, a drop tends to protrude between pillars. The protruding depth is function of surface wettability and increases with the distance between pillars s/d. Then, the pillar height should be greater than this protruding depth of the drop to completely maintain the drop on the top of pillars (see appendix C.2, for more details).

We plotted in the same figure (Figure I.3-7) the data collected on the wetting at high temperature on homogeneous textured surfaces : SiO_2/Pb [14], SiO_2/Sn [15] and on heterogeneous textured surfaces: $Si-SiO_2/Pb$ [15], Mo-Oxides/Sn [84], Fe-Al₂O₃/Zn [85]. In these experiments, the wetting regime was identified by the authors. The obtained results are in good agreement with those at low temperature.

Finally, the pairs {h/d; s/d} of the Fe-SiO₂ textured surfaces used in the present work (Table II.1-3) show that our experimental study will be in the Wenzel state (Figure I.3-7), i.e. the drop lead will be only in contact with the heterogeneous surface Fe-SiO₂.



Figure I.3-7: Wenzel (full marks) and Cassie (empty marks) state as a function of h/d and s/d, experimental transition (solid line) with different wetting systems: homogeneous textured surfaces/water (\Box , \blacksquare) [23], [55], [56], [73], [75], [77], SiO₂/Sn (\bullet) [15], Si-SiO₂/Pb (\bullet) [15], Mo-Oxides/Sn (\bullet) [84], SiO₂/Pb (O) [14], Fe-Al₂O₃/Zn (\bullet) [85], Fe-SiO₂/Pb (\blacktriangle) [this work].

Our work is focused on the wetting of heterogeneous iron/silica substrates with liquid lead. The silica, in the form of square prisms, will be distributed regularly in a square arrangement on iron. Silica is not wetted by liquid lead. For this reason, section I.3 was focused on textured homogeneous solids with low partial wetting to understand the influence of the silica pillar network. The main conclusion of the section I.3 is that a drop of liquid lead put on the silica/iron substrates with the geometrical parameters chosen here will be in Wenzel state. In other words, wetting will depend mainly on the chemical heterogeneity of the substrates. Section I.4 will therefore be devoted to the wetting of heterogeneous textured substrates with non-wetting pillars.

I.4 Wetting of chemically patterned surfaces

I.4.1 Geometry of the solid substrates and wetting conditions

We are now interested in chemically patterned heterogeneous substrates composed of two phases: pattern and substrate. Subsequently noted pattern/substrate as shown in Figure I.4-1. The patterns are square or cylindrical (with a size d and height h) in a square or hexagonal distribution (with s the distance between the patterns).



TCL spreading in d2 TCL spreading in d1

Figure I.4-1: Optical micrographs of a substrate with chemically heterogeneous square patterns [3] and of the two directions of contact angle measurement (d1 and d2).

There is a small number of experiments in literature made in the case of chemically patterned surfaces with square or cylindrical patterns. We found only three sets of experiments at low [65] and high [15], [84] temperature (Table I.4-1 and Table I.4-2).

Table I.4-1: Liquid / solid systems selected for the literature review presented in this work. The solid substrates are heterogeneous textured substrates with non-wetting pillars.

Ref.	Liquid	Solids	Pattern type	Contact angle
[65]	Water (25 nl)	SiO ₂	CS	$\theta_{Y,silica} < 80^{\circ}$
		Silane		$\theta_{Y,silane} \approx 100^{\circ}$
[15]	Tin $(1 \ cm^3)$	Si	CH_{reg}, SH_{reg}	$\theta_{Y,Si} \approx 40^{\circ}$
		Silica		$\theta_{Y,Silice} \approx 120^{\circ}$
[84]	Tin (25 <i>mm</i> ³)	Molybdenum (Mo)	SS	$5 < \theta_{Y,Mo} < 18^{\circ}$
------	----------------------------------	--------------------------	----	----------------------------------
		oxide glass ceramic (GC)		$115 < \theta_Y < 125^\circ$

CS: Cylindrical pillars, Square arrangement, CH_{reg}: Cylindrical pillars, Regular Hexagonal arrangement, SH_{reg}: Square pillars, regular hexagonal arrangement, SS: Square pillars, square arrangement.

Table I.4-2: Geometrical parameters of the solid systems selected for the literature review presented in this work.

Ref.	Pattern type	Pattern size $d (\mu m)$	Pattern space	Pattern height $h(\mu m)$
			s (µm)	
[65]	CS	3,4	2-13	0.8-0.003
[15]	CH_{reg}, SH_{reg}	60	40, 120	0.0028
[84]	SS	60	2.5-60	0.1

For the three studies considered [15], [65], [84] (Table I.4-2), the value of h/d does not exceed 0.1. This means that the liquid drop will be in Wenzel state (Figure I.3-7). In addition, the influence of pillar height is negligible and only the chemical heterogeneity of the substrate will have an influence on wetting.

In these experiments, two different cases should be distinguished depending on whether the pattern is the less wetting substrate or not.

I.4.2 Measured contact angles

The advancing and receding contact angles presented in [15], [65], [84] are shown in Figure I.4-2 and Figure I.4-3 as a function of the surface fraction of the less wetting phase. In Figure I.4-2, patterns are the less wetting phase while in Figure I.4-3 the substrates are the less wetting phase. Beyond the packing limit sf_{pack} [65], the pattern and substrate are inverted. The packing limit is the surface fraction of tangent patterns on substrate: inversion of discontinuity, the patterns begin continuous and substrate begins discontinuous. The packing limit is equal to 1 for square patterns and 0.79 for cylindrical patterns.

First let us consider the case where the patterns are the less wetting phase, Figure I.4-2. In this case, the wettest part of the substrate is continuous and its least wetted part consists of discrete pillars. The receding contact angle is almost constant and is equal to the receding contact angle on the wettest solid. This is because the TCL is pinned by the most wetting part of the substrate,

which is continuous. While the advancing contact angle depends on the surface density of the patterns.

In the second case (Figure I.4-3), the least wetted part of the substrate is continuous and its wettest part consists of discrete pillars. In this case, the advancing contact angle is nearly constant, the *TCL* being pinned by the least wetted part of the substrate. While the receding contact angle depends on the surface density of the patterns or the substrate.



Figure I.4-2: Patterns are less wetting than substrate. Advancing (full marks) and receding (empty marks) contact angles on a chemically pattern surfaces according to the density of the less wetting solid. Data collected from references Naidich et al [84], De Jonghe and Chatain [15] and Raj et al[65].



Figure I.4-3: Substrate are less wetting than patterns. Advancing (full marks) and receding (empty marks) contact angles on a chemically pattern surfaces according to the density of less wetting solid. Data collected from references Naidich et al [84], De Jonghe and Chatain [15] and Raj et al[65].

I.4.3 Influence of measurement direction

In the case of square patches, the triple line can be observed in different directions with respect to the pattern. For example, Naidich et al. [84] studied the influence of the measurement direction on the wetting of patterned surfaces with liquid tin. The triple line was observed in the direction along the side (direction 1, *d*1, Figure I.4-1) and in the diagonal (direction 2, *d*2, Figure I.4-1) of the square patches. The contact angle hysteresis was measured using the sandwich drop method (Figure I.1-6). *SS* type patterned surfaces were composed of non-wetting oxide glass ceramic pillars on a wetting molybdenum substrate (Table I.4-1 and Table I.4-2). Values of contact angles in directions 1 and 2 do not coincide (Figure I.4-4). The advancing contact angles measured are a little higher when the triple line is perpendicular to direction d2 than to direction d1 but the difference in the receding contact angle is negligible.

In our tests, we will measure the contact angles for different positions of the triple line with respect to the substrate pattern, to better understand the influence of texture on the macroscopic contact angle all around the drop.



Figure I.4-4: Influence of measurement directions: direction 1, d1 (circle mark) and direction 2, d2 (triangle mark) on advancing (full marks) and receding (empty marks) contact angles of liquid tin on a chemically oxide glass ceramic / molybdenum surfaces.

Objectives of our work

I.5 Objectives of our work

Our work is devoted to the study of the heterogeneous wetting of iron-silica textured surfaces by liquid lead. In the field of wetting of textured surfaces, the majority of studies in the literature are devoted to the liquid water wetting on homogeneous surfaces. Then, literature review mainly based on the wetting at low temperature was needed.

First, we recalled some general principles that govern wetting as well as the fundamental laws of the wetting phenomenon. We showed that wetting is described mainly by the angle of the drop on the surface at the triple contact line. On non-ideal surfaces (heterogeneous and/or rough), the static contact angle is not unique and in this case, the phenomenon of contact angle hysteresis (advancing and receding contact angles) is important.

Then, we analysed experimental data of wetting of homogeneous and hydrophobic textured surfaces with a contact angle close to 120° (close to that of the Silica/lead system which is around 130°). This analysis showed that contact angle depends on two dimensionless lengths characteristic of the surface texture: the ratio of pillar height and pillar diameter (h/d) and the ratio of the distance between pillars and the pillar diameter (s/d). On the basis of the values of these parameters, all the experimental points follow the same trend and allow to define the two wetting regimes: namely the Cassie state (drop base in contact with the solid surface and gas) and the Wenzel state (drop base in contact only with the solid surface). The clear distribution of experimental data between the two states led us to highlight the experimental transition from one state to another. This experimental wetting transition is the same at high temperature. According to that experimental transition drawn from literature, only the Wenzel state is possible with our textured surfaces, given the couples (s/d, h/d) of the surfaces.

Afterwards, we showed that the size of the pillars and their shape have little influence on the wetting at a given surface fraction of the pillars.

In contrast, there are very few studies on wetting at high temperature on textured surfaces and even fewer on heterogeneous textured surfaces [14], [15], [65]. These studies confirmed the influence of the surface fraction of the defects on wetting and showed a slight influence of the spreading direction on the contact angle.

Thus, the phenomenon of wetting of heterogeneous textured surfaces at high temperature is still a little studied subject and further work is needed.

In this work, we hope to bring some elements likely to advance this subject, or at least to provide some food for thought.

Chapter II: Experimental apparatus and methods

II Experimental apparatus and method

The experimental wetting studies were carried out using an experimental setup based on the dispensed drop technique [1]. A systematic protocol for the preparation and characterization of our samples was set up in order to precisely study the involved parameters in wetting.

In this chapter, the different materials used and the method of their preparation are presented in section II.1. Then, the experimental device used in the wetting experiments (section II.2) will be presented. Afterwards, different techniques and methods to characterize the wetting results will be described (section II.3 and section II.4). The chapter ends with a summary of the different parameters measured for each sample.

II.1 Materials

II.1.1 Liquid metal preparation

As mentioned earlier, the main objective of this thesis is to study the non-reactive wetting of silica / iron patterned surfaces by liquid lead (Pb), which is non-reactive on both iron and silica. The weight of the metal used is determined by the droplet generator of the experimental device. This droplet generator is composed of a cylindrical alumina crucible and a capillary at its bottom with an internal diameter of 2.0 ± 0.1 mm (section II.2.1 for more details). Therefore, the metal weight was chosen to form a liquid droplet with a diameter slightly greater than 2 mm.

The metal lead was supplied by *Alfa Aesar* in the form of a shot (99.9999 wt. %, the principal impurities being silver, calcium and copper). The metal shot is mechanically polished to remove the oxide layers on its surface and to obtain a round lead sphere of mass $m_{Pb} = 100 \pm 5$ mg (i.e., with a diameter of $D_0=2.63 \pm 0.02$ mm).

The physical properties of lead at 450°C used in our experiments are given in Table II.1-1 [86], [87].

	Melting	Density, ρ_{Pb}	Viscosity, μ_{Pb}	Interfacial tension,
	point (° C)	(kg/m^3)	(mPa.s)	$\gamma_{Pb} (mJ.m^{-2})$
Lead (Pb)	327.4	10509	2.02	443

Table II.1-1: Physicochemical properties of lead at 450°C [86], [87].

II.1.2 Solid substrates: tailored model surfaces

In the previous studies performed in our laboratory [1], [2], industrial steels or binary iron / silicon alloys were used for wetting by liquid metals. After annealing and depending on the selected experimental conditions, silicon oxide particles or films were formed on the surfaces by selective oxidation. However, these annealed steel surfaces were too complex to study precisely the influence of the oxide geometrical parameters on wetting by liquid metals. In fact, in this case, the particle sizes and distances between particles are not identical. The shape of the oxide particles and the surface area covered by the oxides also vary according to the orientation of steel grains.

To avoid the influence of the above-mentioned factors on the wettability of steel surfaces by liquid metals, we use model surfaces with controlled distribution of oxide patterns.

In addition to these well-controlled surfaces, pure materials (iron and silica) were also used as references in the experiments.

II.1.1.1) Pure materials

Pure iron

The pure iron used in this study was provided by Goodfellow (99.99 wt.%). Its chemical composition is given in Table II.1-2.

As shown by the Fe-Pb phase diagram (Figure II.1-1), liquid lead does not form intermetallic compounds with iron. In addition, lead and iron are immiscible at the temperature chosen for the wetting experiments, which is 450°C (723 K). The solubility of iron in lead at this temperature is less than 1 ppm.

Table II.1-2: Chemical composition of pure iron used in the experiments as surface reference.

	Manganese	Silicon	Chromium	Titanium
	(Mn)	(Si)	(Cr)	(<i>Ti</i>)
Pure iron (99.99 wt.%)	1 ppm	2 ppm	4 ppm	4 ppm

Thin layer of silica

In addition to pure iron, pure silica was also used as a reference case for wetting of patterned surfaces. For this purpose, a thin 50 nm silica layer was deposited by Plasma Enhanced

Chemical Vapour Deposition (PECVD) on a pure recrystallized iron (99.99 wt.%, *Goodfellow*) in the same way as when preparing patterned surfaces (section II.1.1.2)).



Figure II.1-1: Fe–Pb binary phase diagram [88].

II.1.1.2) Tailored surfaces

Fe / silica patterned surfaces were designed to better understand the influence of the surface area fraction covered by silica and the size of oxide particles on wetting.

The method used is composed of several steps. First, a silicon oxide layer of about 70 nm (amorphous SiO₂ nanofilm), similar to that obtained during recrystallization annealing, was deposited by PECVD on a pure recrystallized iron (99.99 wt. %, *Goodfellow*). The composition of the pure iron used is given in Table II.1-2. To obtain the silica patches, a positive

photosensitive resin (photoresist) and then a photomask with holes corresponding to the targeted pattern were deposited on this silica film. Using UV light treatment, the geometric pattern is transferred to the photoresist by removing it on the exposed area (the mask holes). Subsequently, a chemical etching was performed to remove the silica layer in the same exposed area. Finally, the protective resin was removed from the silica patterns to obtain the desired Fe/silica patterned surface.

This method makes it possible to produce heterogeneous surfaces composed of silica squares, well defined in nature, morphology and stoichiometry. The different tailored surfaces obtained are designated {*d*; *s*} in the following, with $d(\mu m)$ the size of the silica pillars and $s(\mu m)$ the distance between the pillars in the square arrangement (Figure II.1-2).

More information on the method used to fabricate these patterned surfaces can be found in Koltsov *et al.* [3].



Figure II.1-2: Optical micrographs of Fe / silica tailored surfaces with different square silica pillars' size and distribution: (a) {500; 100}, (b) {500; 500}, (c) {100; 100}, (d) {100; 500}. Images gathered from [3].

II.1.1.3) Characterization of the patterned surfaces

Different analytical techniques were carried out by Koltsov *et al.* [3] to characterize the Fe / silica patterned surfaces. The results showed good agreement with the desired surfaces in terms of silica nature and stoichiometry, as well as pattern size, thickness and distribution (Figure II.1-2).

Furthermore, analytical techniques showed the presence of a polycrystalline 25-30 nm thick layer of magnetite (Fe₃O₄) beneath a SiO₂ layer (about 70 nm thick) as shown in Figure II.1-3. This magnetite layer was supposed to be produced by the slight oxidation of the iron substrate during silicon oxide deposition. However, this magnetite sublayer between silica and iron does not change the wetting properties of the pattern substrates, because, like silica, magnetite is not wetted by liquid lead [89].

The height of the silicon oxide pillars was found to be slightly higher than the total thickness of SiO_2 and Fe_3O_4 layers, varying from 95 to 120 nm depending on the sample. The difference was explained to be related to some over pickling of the Fe surface during etching.





This technique provides tailored surfaces which well reproduce the type and chemistry of silicon oxide layer formed during recrystallization annealing: stoichiometric and amorphous silicon dioxide film. The obtained film thickness is slightly higher, but close enough to the one observed during recrystallization annealing.

II.1.1.4) Geometrical parameters of the investigated silica-patterned iron substrates

Using the above-described technique, ten patterned surfaces with different silica surface coverages have been used for the wetting experiments. The samples can be classified into three groups: low (3%), moderate (25%) and high (~70%) silica surface coverage f:

$$f = \frac{1}{\left(1 + \frac{s}{d}\right)^2} \tag{II.1.1}$$

For each surface coverage, three to four different patterns were considered (Table II.1-3). Thus, the influence of the oxides' surface coverage and size on wetting by liquid lead can be studied with these samples.

Table II.1-3: Fe/silica tailored surfaces elaborated by the PECVD method and used in this work: silica pillar size, inter-pillar distance and surface coverage. A {d; s} patterned sample has a pillar size of d μ m and an inter-pillar distance of s μ m.

Patterning samples	Pillar size	Inter-pillar	Silica covering
$\{d, s\}$	d(µm)	distance s(µm)	yield, $f(\%)$
{5; 20}	5	20	4
{20; 100}	20	100	3
{100; 500}	100	500	3
{5;5}	5	5	25
{20; 20}	20	20	25
{100; 100}	100	100	25
{500; 500}	500	500	25
{20; 5}	20	5	64
{100; 20}	100	20	69.4
{500; 100}	500	100	69

In the following chapters, we will describe the experimental device used in our tests: the wetting experiments were performed by means of the dispensed drop technique.

II.2 Experimental device

We performed dynamic wettability experiments using the dispensed drop technique, a widespread method in wettability studies [4], [90]. We used the experimental device (Figure II.2-1), set up and used by Zaïdi [1] and Diawara [2] during their PhD thesis.



*Saphir: $N_2 + 5$ vol.% H_2

Figure II.2-1: Schematic representation of the wettability experimental device (dispensed drop method) [93].

II.2.1 Description of the experimental setup

The experimental device (Figure II.2-1) mainly consists of a resistance furnace (*Pyrox*), a gas supply, a liquid metal generator and a high-speed CMOS camera (*pco.1200 hs*). The camera is connected to a computer allowing to film and record the dynamic spreading of the liquid drop.

The reducing gas atmosphere needed for the wetting experiments is first prepared. A vacuum pump is used to evacuate the air initially present in the furnace chamber and to establish a primary vacuum (approximately 3.10^{-2} mbar). A reducing atmosphere is then introduced in the device, by means of a sweep gas composed of nitrogen (N₂) and 5 vol.% hydrogen (H₂) and containing less than 3 ppm of water and 2 ppm of oxygen (supplied by *Air Liquide*). The flowrate of this sweep gas was maintained at $1.25 \times 10^{-5} \text{ m}^3 \text{ s}^{-1}$ at standard conditions of pressure and temperature (0°C, 100 kPa) for 2 h, before the beginning of the experiments. With this preparation, the reached partial pressure of water in the gaseous atmosphere was as low as possible (of the order of 2 Pa, i.e. a frost point of -55°C).

The temperature of the sample is measured by two type-*K* thermocouples located under the sample holder (Figure II.2-1). The frost point of the gas is measured at the furnace outlet using an alumina moisture probe (Panametrics).

The whole wetting experiments are carried out with the constant flowrate of the sweep gas described before. In this reducing atmosphere, a liquid metal droplet is formed at the wetting temperature by means of a drop generator. It consists of a cylindrical crucible made of alumina. It is equipped at its bottom by an alumina capillary, measuring 10 mm in length, 2 ± 0.1 mm in internal diameter and 4.15 ± 0.01 mm in external diameter. The liquid metal is dispensed on the sample placed on the sample holder under the drop generator, using an overpressure of N₂-H₂ gas.

The furnace is equipped with two viewing ports on both sides. On one side, a constant light source is provided by means of a lamp (KL 2500, liquid-crystal display, LCD). On the other side, the camera is set to film the whole wetting experiment inside the furnace. The high-speed CMOS camera is programmed with a recording speed of 1000 frames per second and a resolution of 780 x 501 pixels for each image.



II.2.2 Experimental procedure

Figure II.2-2: Sample temperature and furnace frost point as a function of time during an experiment: the metal to be melted is introduced into the crucible at point 1 and the formed metal drop is extruded at point 2 [93].

Before each experiment, the desired temperature profile is set up using a programmable temperature controller (*Pyrox*).

Before introducing the sample in the furnace, the horizontality of the sample holder is adjusted and checked using a spirit level. Then, the sample is placed on this sample holder in two different ways with respect to the camera axis (Figure II.2-3): the movement of the triple contact line (*TCL*) can be filmed in a direction parallel to the side of the squares (direction d1) or to the diagonal of the squares (direction d2).



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Figure II.2-3: The two positions of the sample relative to the camera axis before the experiment.

Afterwards, the metal shot is introduced in the spherical valve V4 located outside the furnace and directly connected to the drop generator (Figure II.2-1).

The sample temperature and the furnace frost point are measured during the whole experiment (Figure II.2-2). The experimental protocol can be divided into three different stages: preparation of the gas atmosphere, annealing at 850°C and dynamic wetting at 450°C.

In the first stage, a primary vacuum with a pressure of about 3.10^{-2} mbar was established using the vacuum pump (Figure II.2-1). The sweep reducing atmosphere composed of N₂ and 5 vol. % H₂ is introduced in the furnace chamber at a flowrate of 1.25×10^{-5} m³ s⁻¹ at standard conditions of pressure and temperature (0°C, 100 kPa) and maintained until the end of the wetting experiment. After 2 h, the frost point in the furnace is less than -50 °C.

The sample then undergoes a series of heat treatments according to the temperature profile given in Figure II.2-2. The sample is annealed at a temperature of 850°C in one hour. During this step, the furnace frost point increases when the temperature reaches about 200°C. This is attributed to the water desorption initially present on the furnace walls. The aim of this annealing at high temperature is to reduce the native iron oxide film. After the annealing process, the sample is cooled down to a temperature of about 450°C and maintained at this temperature for 25 min to ensure isothermal conditions in the system. At the end of this stage, the furnace frost point is about -60°C (Figure II.2-2).

Then, the dynamic wetting experiment is carried out at a constant temperature of 450°C, as in industrial conditions. The metal shot is brought into the drop generator in the furnace by opening the spherical valve V4 (point 1 in Figure II.2-2). The metal shot is completely melted after about 5 min. An overpressure is applied above the crucible to dispense the liquid metal drop. The higher the overpressure, the higher the impact velocity of the liquid metal on the sample (point 2 in Figure II.2-2). An overpressure of 6-10 mbar was used to dispense the drop in our experiments.

Due to this overpressure, the liquid metal drop is released on the sample. The whole dynamic wetting, from the drop fall, the spreading to the final state, are filmed and recorded using the high-speed camera, at 1000 images per second. Figure II.2-4 illustrates an example of a spreading sequence of a liquid lead on a {100; 100} patterned surface.

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Figure II.2-4: Sequence of a liquid lead spreading on a {100, 100} patterned surface.

II.3 Image treatment methods

At the end of each experiment, the camera recorded hundreds of images (several hundred megabytes in size) with a resolution of 501x780 pixels for each image. These images are then processed to obtain the macroscopic wetting parameters, namely the spreading diameter D, the maximum height H_d , the left and right contact angles θ_L and θ_R . The processing of these images by hand can be time consuming and very tedious. In addition, depending on the experimenter's capabilities and environmental conditions (light in the room, screen quality), the results of manual measurement may vary. Thus, to reduce errors related to the experimenter, several algorithms have been developed with the MATLAB® software and its image processing toolbox to automate the measurements of wetting parameters.

II.3.1 Image pre-processing

Before processing each series of images, the image scale (ps_{im}) in pixels / mm is measured using as a reference the external diameter of the capillary at the bottom of the drop generator (size 4.15 ± 0.02 mm).

In our experiments, the camera was positioned with a slight inclination α_{cam} (less than 3°, measured with a Bosch inclinometer, DNM 60 L Professional) with respect to the plane parallel to the sample surface, so that the drop and its reflection are filmed to facilitate the determination of the drop contact line on the sample (Figure II.3-1a). In the image plane, the triple line can be slightly tilted α_{TCL} (less than 4°) due to a slight tilt of the camera or sample holder. Consequently, the precise position of the triple line is determined using the drop reflection (Figure II.3-1a). In the following image processing, the triple line is considered as a straight line of equation:

$$Y = a_{tcl}X + b_{tcl} \tag{II.3.1}$$

Once the drop and its triple line were identified, the image was processed to extract the drop contour (Figure II.3-1b). To do this, an edge method was used that follows a path of rapid change in image intensity. To date, the most powerful method of edge-detection that MATLAB® provides is the "Canny" method. In this method, two different thresholds are used to detect strong and weak edges. In our case, strong edges are taken into account but also weak edges if they are connected to strong edges. This method provides the complete drop contour as shown in Figure II.3-1b.

Then, the geometric parameters of the drop were calculated: spreading diameter and maximum height (section II.3.2), impact velocity (section II.3.3), mean spreading velocity (section II.3.4) and left and right contact angles (section II.3.5).



Figure II.3-1: Image pre-processing for length measurements. a) Initial image with the capillary, b) Drop contour (obtained using the "Canny" method of MATLAB® software) with the triple line position, the two extreme points on the contour and the highest point. In b), there are 52 pixels per 1 mm.

II.3.2 Spreading diameter and height of the droplet

Method of measurement

If the solid substrate is homogeneous or heterogeneous with small defects compared to the capillary length, the contact surface between the droplet and the solid substrate is a circle, in the case of a low droplet spreading velocity. The spreading diameter is the diameter of this contact surface. The location of the triple line is used to determine the two extreme points to the left and right of the triple line, with the pixel coordinates (X_{lTCL}, Y_{lTCL}) and (X_{rTCL}, Y_{rTCL}) respectively. The spreading diameter is therefore given by a simple distance calculation:

$$D = \sqrt{(X_{rTCL} - X_{lTCL})^2 + (Y_{rTCL} - Y_{lTCL})^2} \times \frac{1}{ps_{im}}$$
(II.3.2)

In addition, the drop shape is used to determine the highest point of the drop (X_{hdrop} , Y_{hdrop}). The slight inclination of the triple line with respect to the horizontal plane is taken into account in the calculation of the droplet maximal height (Figure II.3-1b):

$$H_d = \frac{\left|a_{tcl} \times X_{hdrop} - Y_{hdrop} + b_{tcl}\right|}{\sqrt{1 + a_{tcl}^2}} \times \frac{1}{ps_{im}}$$
(II.3.3)

The droplet diameter and maximum height are made dimensionless using a reference diameter D_0 (mm). This reference diameter corresponds to the diameter of the liquid metal droplet supposed to be spherical (density ρ_{Pb}) with the same weight (m_{Pb}) as the solid metal shot used in the wetting experiments.

$$D_0 = \left(\frac{6 \times m_{Pb}}{\pi \times \rho_{Pb}}\right)^{1/3} \tag{II.3.4}$$

Error measurements linked to the slight inclination of the camera

If the inclination of the triple line is negligible $(Y_{rTCL} \approx Y_{lTCL})$ in the image plane, the droplet maximal height is simply given by:

$$H_{d}' = \left| Y_{rTCL} - Y_{hdrop} \right| \times \frac{1}{ps_{im}} \tag{II.3.5}$$

For a tilted contact line of α_{TCL} , the two expressions of the maximal heights of the droplet (Eq. (II.3.3) and Eq.(II.3.5)) are related:

$$\frac{H_d'}{H_d} = \cos \alpha_{TCL}$$
(II.3.6)

In our experiments, the tilt angle of the contact line was less than 4° , $H_d' = 0.9976H_d$, then the effect of the triple line inclination is negligible on the maximal height of the drop.

Moreover, the effect of the camera inclination on the maximal height of the droplet is also negligible. In fact, the slight inclination of the camera ($\alpha_{cam} = 3^\circ$) reduces the value of maximal height of $1 - \cos \alpha_{cam} \approx 0.0013$ and then will be neglected.

Error measurements of the image processing

In order to validate the image processing protocol, we filmed a spherical steel ball under the same conditions as in the wetting experiments. The diameter of this ball was $D_{ball} = 3.28 \pm 0.02$ mm, which is close to the diameter of the lead drop $D_0 = 2.63$ mm. The image obtained (first image in Figure II.3-2) is an almost perfect sphere (the diameter is 163 pixels in the horizontal direction and 165 pixels in the vertical direction, i.e. a distortion less than 2%). Then, the ball image was used to generate theoretical spherical caps with contact angles ranging from 5° to 170° (Figure II.3-2). For a given contact angle θ , the height H_d and diameter D of the spherical cap are given by:

$$H_{d} = \frac{D_{ball}}{2} (1 - \cos \theta)$$

$$D = D_{ball} \sin \theta$$
(II.3.7)

Subsequently, we applied the algorithms developed to these images. The measurement uncertainty is illustrated in Figure II.3-3. For each spherical cap, the calculated diameter and height were compared to the target values given by Eq.(II.3.7).

In Figure II.3-3a, the uncertainty in the contact diameter $(\Delta D/D_0)$ decreases when the contact surface increases and then the uncertainty depends strongly on the difficulty to position the triple contact line when the contact surface is small. An uncertainty greater than 0.08 was obtained for a small contact diameter $\left(\frac{D}{D_0} < 0.2\right)$. In our experiments on patterned surfaces, $\frac{D}{D_0} > 0.2$ and in this case, the maximum uncertainty is about 0.08 (Figure II.3-3a), which will be then considered as the uncertainty in the measurement of the drop diameter.

As the measurement of the drop height is not related to the determination of the triple line, the uncertainty $(\Delta H_d/D_0)$ is therefore an order of magnitude less than the uncertainty on the diameter (Figure II.3-3b). The maximum uncertainty is 0.007, which will be considered as the uncertainty of the maximum height measurement.

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Figure II.3-2: Theoretical drops for the validation of the measurement methods developed. The first image was recorded in the same conditions as in the wetting experiments.

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Figure II.3-3: Uncertainty in the length measurements estimated with the reference images of spherical caps as a function of contact angle. (a) Dimensionless contact diameter, (b) dimensionless drop height.

II.3.3 Impact velocity

The impact velocity is the velocity of the droplet when it comes into contact with the solid surface after falling from the droplet generator. The initial kinetic energy of the droplet, which is a function of its impact velocity, is an important parameter for the study of dynamic wetting.

$$V_o = V_{fall} + \frac{1}{2}gt_{fall} \tag{II.3.8}$$

with V_{fall} the average velocity, t_{fall} the fall time and g the gravity acceleration. The average velocity (V_{fall}) is determined from the images of the film. In the example of Figure II.3-4, the average velocity is measured from the position of the droplet when it exits the capillary tube (t = 1 ms) and the position of the droplet just before its contact with the solid substrate (t = 4 ms): $V_{fall} = \frac{-h_1 + h_5}{4-1}$. The uncertainty in the measurement of the impact velocity is estimated to $\pm 0.02 \text{ m/s}$ from the uncertainty in the measurement of h_5 (linked to the uncertainty in the pixels' number and size).



Figure II.3-4: Example of an image sequence used in the determination of the impact velocity of the droplet.

The contribution of gravity to the impact velocity is negligible compared to the droplet velocity at the capillary tube outlet (less than 5% in all cases). In the case of Figure II.3-4, $V_o = 0.78$ m/s with 0.03 m/s due to the contribution of gravity or 3.8%. Therefore, in the experiments performed here, the impact velocity and then the kinetic energy will depend mainly on the overpressure applied in the droplet generator.

II.3.4 Mean spreading velocity

For continuous displacement, the mean spreading velocity of the triple line is the derivative of the spreading radius $\frac{1}{2} D(t)$ with respect to time t. Since we only have discrete data, i. e. two consecutive images of the film being separated by 1 ms, the spreading velocity U, at time t_i , is given by the following equation:

$$U(t_i) = \frac{dD(t)}{2dt} \bigg|_{t=t_i} \approx \left. \frac{D(t_{i+1}) - D(t_{i-1})}{2(t_{i+1} - t_{i-1})} \right|$$
(II.3.9)

Considering a two-pixel error in the measurement of the spreading diameter, the uncertainty in the measurement of the spreading velocity is estimated to be \pm 0.02 m/s. An example of the evolution of the spreading velocity versus time is given in Figure II.3-5.



Figure II.3-5: Spreading velocity of liquid lead on {20, 20} patterned-surfaces as function of time and droplet initial impact velocity.

II.3.5 Left and right contact angles

High-speed camera operating conditions

For liquids with a low viscosity like liquid metals, the contact angle measurements can be obtained precisely, only in the case of low spreading velocity of the triple line. In the case of rapid spreading, the contact angle measurements are more difficult and often lead to uncertainties of several degrees. This may be due to a number of factors, including the deformation of the liquid surface and the difficulty in detecting correctly the triple contact line position due to its high spreading rate (about 1 m s^{-1} , Figure II.3-5).

In order to detect the position of the triple line as well as possible, the distance travelled by the triple line during the camera exposure time must be less than the size of one image pixel. If these two distances are of the same order of magnitude, a systematic error of one pixel is made, causing a high uncertainty in the contact angle. In order to solve this problem, a high-speed camera with a reduced exposure time can be used. In our experiments, the exposure time of the camera was set at 0.5 μ s. Since the maximum initial velocity of the triple line is around 1 m/s, the triple line crosses 0.5 μ m during this time, which is much less than the pixel size of around 15 μ m of the produced image from our camera.

Notwithstanding, the image should also be centred on the triple line, with a large magnification to obtain the highest possible image resolution. In our experiments, the left and right contact angles must be determined at the same time as the spreading diameter of the droplet. Therefore, it is not possible to zoom in on the moving contact line at only one side. However, with the conditions chosen, the pixel size of 15 μ m is sufficient to measure an apparent macroscopic contact angle, as in conventional wetting experiments.

Image processing to determine the left and right contact angles

The method used to measure the left and right contact angles was developed and explained by Vadillo [91]. To reduce the calculation time, a limited number of pixels close to the triple line are taken into account on the drop contour when measuring the contact angle (5-30 pixels corresponding to 0.1 to 0.5 mm of contour length). An example of the pixels selected near the triple line is shown in red in Figure II.3-6b. Then, all possible lines that cross all selected pixels are determined. The mean contact angles are calculated on the left and right. The mean contact angle corresponds to the mean tangent (in blue in Figure II.3-6b) between the two extreme lines (lines with minimum and maximum slopes) of all lines crossing the selected pixels.



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Error measurements of the image processing

To validate the contact angle measurement method, the contact angles were measured on reference images of spherical caps (Figure II.3-2). For each spherical cap, the calculated angle was compared to that of the target. The measurement uncertainties on the left and right are shown in Figure II.3-7.

In Figure II.3-7, the uncertainties on measurements at low (5°) and high (>150°) contact angles are high and the measurements are not accurate. However, in our experiments, the contact angles are between 20° and 150°. In this case, the difference between the calculated contact angle and the target contact angle is between $+5^{\circ}$ and -6° . Thus, a systematic error of ± 5 is considered on the measurement of the left and right contact angles and then on the mean contact angle.



Figure II.3-7: Uncertainty in the measurements of left and right contact angles estimated from the reference images of spherical caps.

Figure II.3-8: Comparison of dynamic contact angle measurements obtained from the developed algorithms (in blue) and by hand with the ImageJ software (in red). Two different iron / silica patterned surfaces are used for this validation: {20; 20} with a silica surface coverage of 25% (full marks) and {20; 5} with 64% silica surface coverage (empty marks).

presents two examples of the wetting of patterned surfaces {20; 20} and {20; 5} by liquid lead. The contact angles (average of the left and right contact angles) obtained with the method developed here are compared to those obtained manually. In both cases, the differences between the two measurements lie in the uncertainties of the measurements determined in Figure II.3-7 $(\pm 5^{\circ})$.



Figure II.3-8: Comparison of dynamic contact angle measurements obtained from the developed algorithms (in blue) and by hand with the ImageJ software (in red). Two different iron / silica patterned surfaces are used for this validation: {20; 20} with a silica surface coverage of 25% (full marks) and {20; 5} with 64% silica surface coverage (empty marks).

II.3.6 Contact angle hysteresis

The experimental device used in this work was designed to study the dynamic spreading of liquid metals at high temperature but not specifically to measure the contact angle hysteresis with the methods described in section I.1.6.2. However, the change in spreading diameter and contact angle over time can be used to determine this contact angle hysteresis θ_a and θ_r . In our tests, during the first milliseconds, the spreading diameter increases up to its maximum value and then decreases, indicating a receding of the droplet triple line. After that, the spreading diameter increases again. Finally, it reaches its final value after approximatively 100 ms of oscillations (Figure II.3-9). The contact angle hysteresis can be determined using the corresponding variation of the contact angle over time.

Two methods were evaluated, the first one using the droplet behaviour at the maximum spreading diameter and the second one using contact angles during the drop receding and advancing.



Figure II.3-9: Contact diameter and angle of lead drop on {100; 20} patterned surface.

Method using the maximum spreading diameter

A first approach is to examine what happens at the maximum spreading diameter. Indeed, at this moment, the droplet is pinned at its maximal spreading diameter for a few milliseconds while the contact angle takes several values. There is therefore a variation of the contact angle at zero spreading velocity, i.e. a contact angle hysteresis.

This contact angle hysteresis can be determined directly from the film images or the graph of the evolution of the dynamic contact angle as a function of spreading velocity for U = 0 (Figure II.3-10).



Figure II.3-10: Overall shape of dynamic contact angle as a function of spreading velocity. Inspired by [92].

For the wetting of heterogeneous patterned surfaces by liquid lead, this technique does not always give satisfactory results. Indeed, due to the specific shape of the texture, during the first step of spreading, the triple contact line mainly spreads on pure iron and the hysteresis thus measured is close to that of pure iron.

Method using the stick-slip motion of the triple line

The contact angle hysteresis can be determined using the stick-slip motion of the triple contact line. Chatain *et al.* [14] have already described this stick-slip motion for surfaces with regular patterns, highlighted by the sandwich drop method.

Figure II.3-11 shows the wetting of the {5; 20} sample by liquid lead. After impact on the sample, the droplet spreads to its maximum spreading diameter and then recedes. During its receding, the droplet stops at t = 16 ms. The spreading diameter remains constant while the contact angle decreases to reach the receding contact angle. At this point, the spreading diameter decreases again. In addition, around t = 25 ms, the drop stops again and the contact angle increases and reaches the advancing contact angle. The spreading diameter then increases. Thus, the receding and advancing contact angles can be determined using this technique.

However, as discussed in chapter III, the stick slip motion is not evident on some patterned surfaces, particularly on samples with high silica coverage. In this case, the receding θ_{dr} and

advancing θ_{da} contact angles are measured only by considering the first receding and second advancing of the drop.



Figure II.3-11: Example of contact angle hysteresis measurement using the stick-slip motion. The drop undergoes a series of stick-slip phenomena. The case of {5; 20} patterned sample.

The contact angle hysteresis obtained by the mean of the two procedure will be compared in chapter III.

II.4 Characterization of the solidified droplets

Due to the heterogeneity of patterned surfaces, the shape of the droplet and therefore its spreading diameter and contact angle may vary from one point to another on the surface. The shape of the solidified droplets was observed in order to investigate the influence of the position of the triple line with respect to the texture. Lateral (section II.4.1) and top (section II.4.2) views of the droplets were observed.

II.4.1 Lateral view of the solidified droplets

The droplet shape and the left and right contact angles are measured as a function of the angle of view using the solidified droplet. To do this, after the wetting experiments at high temperature, the sample with the liquid lead droplet is cooled to room temperature. It is then placed on a rotating microscope stage and a lateral view of the drop is recorded for different angles of view using a high-resolution camera (v310, Phantom), a macro lens (AF Zoom-Micro Nikkor 70-180 mm f/4.5-5.6D ED, Nikon) and a light source (lamp KL 2500 LCD) (Figure II.4-1). Forty images with a resolution of 800 x 1280 pixels were taken, corresponding to angles of view α_v from 0° (when the side of the silica pattern is perpendicular to the camera axis) to 360° with a 9° step.



Figure II.4-1: Setup for the measurements of the spreading diameter and left and right contact angles of the solidified droplet.
The recorded images are processed to measure the spreading diameter D^l and the mean contact angle θ^l of the solidified drop. The effect of the observation direction on the droplet shape can then be visualized, as shown in Figure II.4-2 for a {5; 5} patterned surface.

These measurements will then allow to study the elongation of the drop in several directions as well as the dispersion of the contact angle on the solidified drop.



Figure II.4-2: View of the drop shape in lateral view on the {5, 5} sample. (a) Dimensionless drop diameter, (b) drop contact angle as a function of angle of view.

Measurement uncertainty of contact diameter

An uncertainty of two (2) pixels is considered in the measurement of the contact diameter. On these images, the scale is about 45 pixels/mm. Then the measurement uncertainty of the contact diameter is about ± 0.04 mm. Subsequently the maximum uncertainty in D/D₀ at lateral view is fixed to ± 0.04 .

The uncertainty in the measurement of contact angle remains to ± 5 as in the images from the spreading dynamics.

II.4.2 Top view of the solidified droplets

The lateral view of the solidified droplet makes it possible to obtain its shape, but, due to the heterogeneity of our surfaces, the triple line of the droplet does not remain perfectly circular. A top view of the drop is therefore required to calculate the circularity of the triple line (section II.4.2.1) and to obtain the position of the triple line with respect to the texture (section II.4.2.2).

This top view is relevant only when the contact angle is lower than 90° .

II.4.2.1. Criterion of the drop circularity

Figure 4.3a shows the example of a solidified lead drop on a patterned surface {500; 500}. The image is obtained by means of a modular stereo microscope (Zeiss Stereo Discovery V12 with motorized 12x zoom). The image is zoomed as much as possible (with more than 100 pixels/mm) to extract both the drop shape and a position of the square silica.

The top view of the droplet (Figure II.4-3a) is processed as before (section II.3.1) to obtain the triple line contour as a set of discrete pixel points of coordinates (x_i, y_i) (Figure II.4-3b). Then, the contact surface area A_{drop} of the drop on the solid sample is calculated with the number of pixels on the contact surface.

Knowing the coordinates of the discrete points of the triple line, the coordinates of the centre of mass of the contact surface of the drop G_{drop} (Figure II.4-3c) are given by:

$$G_{drop}(x) = \frac{\sum_{i=0}^{n_p-1} (x_i + x_{i+1})(x_i y_{i+1} - y_i x_{i+1})}{3\sum_{i=0}^{n_p-1} (x_i y_{i+1} - y_i x_{i+1})}$$
(II.4.1)
$$G_{drop}(y) = \frac{\sum_{i=0}^{n_p-1} (y_i + y_{i+1})(x_i y_{i+1} - y_i x_{i+1})}{3\sum_{i=0}^{n_p-1} (x_i y_{i+1} - y_i x_{i+1})}$$

where n_p is the number of pixels on the drop contact line.

The centre of mass is then used to determine the circle closest to the triple line, called the optimal circle. First, the minimum D_{min}^t and maximum D_{max}^t Feret diameters of the drop contact line are calculated. Then, the optimal circle diameter D_{opt}^t within the minimum-maximum Feret diameters (Figure II.4-3c), is obtained by minimizing the area of the symmetrical difference between the drop contact area and the circle surface (Figure II.4-3d).



Figure II.4-3: Drop shape in top view for calculating the circularity criterion. Case of a lead drop on a {500; 500} patterned surface. a) Original drop image using an optical microscope, b) extraction of the drop shape with pixel coordinates, c) contour of the triple line and optimal circle obtained, d) symmetrical difference between the optimal circle and the drop contact line.

If the drop contact area and the optimal circle are defined with a set of pixels Ψ_{drop} and Ψ_{cth} respectively, the symmetrical difference Ψ_{diff} between the two sets of pixels is defined as the set of pixels that belong to one and only one of the two sets of pixels ($\Psi_{diff} = \Psi_{drop} \Delta \Psi_{cth}$) (Figure II.4-3d). Then, the area of this symmetrical difference A_{diff} is calculated again with the number of pixels it contains.

The circularity criterion τ_c is defined as the ratio between the area of the symmetrical difference A_{diff} and the area of the drop contact on the solid sample A_{drop} .

$$\tau_c = \frac{A_{diff}}{A_{drop}} \tag{II.4.2}$$

If the contact surface between the droplet and the solid substrate is a circle, the symmetrical difference does not contain pixels, i.e. $A_{diff} = 0$ and consequently the circularity criterion $\tau_c = 0$. Conversely, this criterion tends towards 1 in the case of an ellipse with very distant foci. The latter case corresponds to a drop very spread in one direction on the solid.

Table II.4-1 shows the initial diameter D_0 , the maximum D_{max}^t and minimum D_{min}^t Feret diameters of the drop, the diameter of the optimal circle diameter D_{opt}^t , the area of the symmetrical difference Ψ_{diff} as well as the circularity criterion τ_c for two cases: a perfect circle of 2.50 mm diameter and the solidified drop of the example in Figure II.4-3 (liquid lead on {500; 500} sample).

Table II.4-1: An example of the results of the calculation of the circularity criterion (perfect circle and drop on {500; 500} sample)

Sample	D ₀ (mm)	D ^t _{max} (mm)	D ^t _{min} (mm)	D ^t _{opt} (mm)	Ψ_{diff} (mm ²)	$ au_c$
Perfect circle	2.50	2.50	2.50	2.50	0.0043	8.69.10 ⁻⁰⁴
{500; 500}	2.63	3.78	3.59	3.65	1.1252	0.1074

As expected, the circularity criterion is close to zero for the reference case of the perfect circle, whereas the triple line of the example which seems well deformed has a circularity criterion of 0.1.

Measurement uncertainty

An uncertainty of 5 pixels is considered in the detection of the drop shape due to the difficulty to extract the drop shape from top images. On these images, the scale is at least 100 pixels/mm. Then the maximum uncertainty of the contact diameter measurement is about ± 0.05 mm. Subsequently the maximum uncertainty in D/D_0 measurement at top view is fixed to ± 0.04 .

II.4.2.2. Position of the triple line on the textured surface

The contact angles measured on patterned samples, with a low or moderate silica surface fraction, were found to be very close to the contact angle on pure iron. This behaviour could be explained by the fact that the drop is pinned by pure iron during spreading (chapter III). To prove this, it is necessary to position the triple contact line with respect to the surface patterns. The position of the droplet triple line on patterned surfaces is reconstructed from the top view. Let us take again the case of the solidified drop on the patterned surface {500; 500} (Figure II.4-3). In Figure II.4-3a, it is possible to distinguish both the contact surface between the drop and the solid substrate and the patterns of the surface. Both are extracted from the photograph by image analysis (Figure II.4-4a). As the silica pillars are evenly distributed over the surface, the position of the liquid metal droplet with respect to the texture can be precisely reconstructed. Figure II.4-4 shows the reconstruction of the drop contact line with respect to the texture together with the optimal circle calculated as explained in section II.4.2.2.

From this reconstruction, the surface area fraction covered by silica $(f_{silica})_{surf}$, the triple contact line fraction on silica $(f_{silica})_{tcl}$ and the corresponding contact angles θ_{surf} and θ_{tcl} (Eq. (I.2.4) and Eq. (I.2.6)) are calculated in Table II.4-2.

However, this reconstruction is very tedious for small patterns where it is almost impossible to have both the whole drop shape and a silica pattern. Therefore, this reconstruction was only performed on the samples with enough large pattern size: {100; 500}, {100; 100} and {500; 500}. And, as we will explain later in chapter III, if the drop is large enough in relation to the texture size, the effect of the pattern size is negligible at equilibrium.

Table II.4-2: Fractions of silica and corresponding angles on reconstructed triple contact line on {500; 500} patterned surface.

Sample	(f _{silica}) _{surf}	$(f_{silica})_{tcl}$	$\theta_{surf}(^{\circ})$	$ heta_{tcl}(^{\circ})$
{500; 500}	0.20	0.29	71	77
Optimal circle	0.24	0.19	74	70



Figure II.4-4: Reconstruction of a solidified metal drop and the corresponding optimal circle on a patterned surface. Position of the triple contact line of a drop on {500; 500} patterned surface.

II.5 Conclusion

To study the influence of oxide size and distribution on non-reactive wetting by liquid metal, we used well-defined surfaces. A lead drop was used because it does not react with both iron (substrate) and silica (pattern). In addition to patterned surfaces with different sizes and distributions, pure materials were used. These choices led to oxide surface fractions ranging from 0 to 1.

For the experimental wetting study, the dispensed drop technique was used in order to investigate the entire dynamic spreading of the drop from its fall to its final state. Dynamic spreading was recorded using a high speed-camera with 1000 images per second for 750 x 500 pixels in each frame.

Then, the different image processing methods were used to characterize the images obtained, such as the spreading diameter and the contact angle and the maximum droplet height. The solidified drops were also characterized. The circularity criterion of the drop / substrate contact surface was estimated and the triple contact line was positioned on the sample with respect to the patterns, on as many samples as possible.

For each sample, the measured parameters are summarized in Table II.5-1.

Table II.5-1: Summary of the parameters measured for each sample and for the different silica area fractions.

Samples with low silica area fraction									
Samples	Fe	{5; 20}	{20; 100}	{100; 500}					
	0	4%	3%	3%					
Dynamic parameters									
Spreading direction, d1 and d2	-	Y ¹	Y	Y					
Impact velocity, V_0	Y	Y	Y	Y					
Contact diameter, $(D/D_0)(t)$	Y	Y	Y	Y					
Maximal height, $(H_d/D_0)(t)$	Y	Y	Y	Y					
Contact angle, $\theta(t)$ (°)	Y	Y	Y	Y					
Spreading velocity, $U(t)$ (m/s)	Y	Y	Y	Y					
Contact angle hysteresis, θ_r , θ_a (°)	Y	Y	Y	Y					

	Lateral	view									
Contact diameter, $(D^l/D_0)(\alpha_v)$	Y	Y	Y	Y							
Contact angle, $\theta^{l}(\alpha_{v})$ (°)	Y	Y	Y	Y							
Top view											
Circularity criterion, τ_c	Y	Y	Y	Y							
TCL reconstruction relative to the	-	N ²	N	Y							
sample pattern											
Samples with moderate silica area fraction											
Samples	{5;5}	{20; 20}	{100; 100}	{500; 500}							
	25%	25%	25%	25%							
D	ynamic pa	rameters									
Spreading direction, d1 and d2	Y	Y	Y	Y							
Impact velocity, V_0	Y	Y	Y	Y							
Contact diameter, $(D/D_0)(t)$	Y	Y	Y	Y							
Maximal height, $(H_d/D_0)(t)$	Y	Y	Y	Y							
Contact angle, $\theta(t)$ (°)	Y	Y	Y	Y							
Spreading velocity, $U(t)$ (m/s)	Y	Y	Y	Y							
Contact angle hysteresis, θ_r , θ_a (°)	Y	Y	Y	Y							
	Lateral v	view									
Contact diameter, $(D^l/D_0)(\alpha_v)$	Y	Y	Y	Y							
Contact angle, $\theta^{l}(\alpha_{v})$ (°)	Y	Y	Y	Y							
	Top vi	ew									
Circularity criterion, τ_c	Y	Y	Y	Y							
TCL reconstruction relative to the	N	N	Y	Y							
sample pattern											
Samples w	ith high si	lica area fract	ion								
Samples	{20; 5}	{100; 20}	{500; 100}	Silica							
	64%	69%	69%	100%							
D	ynamic pa	rameters									
Spreading direction, d1 and d2	Y	Y	Y	Y							

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Impact velocity, V_0	Y	Y	Y	Y				
Contact diameter, $(D/D_0)(t)$	Y	Y	Y	Y				
Maximal height, $(H_d/D_0)(t)$	Y	Y	Y	Y				
Contact angle, $\theta(t)$ (°)	Y	Y	Y	Y				
Spreading velocity, $U(t)$ (m/s)	Y	Y	Y	Y				
Contact angle hysteresis, θ_r , θ_a (°)	Y	Y	Y	Y				
Lateral view								
Contact diameter, $(D^l/D_0)(\alpha_v)$	Y	Y	Y	Y				
Contact angle, $\theta^{l}(\alpha_{v})$ (°)	Y	Y	Y	Y				
	Top vi	ew						
Circularity criterion, τ_c	Ν	N	Ν	Ν				
TCL reconstruction relative to the	N	N	N	N				
sample pattern								

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¹Y: Yes, measurement done ²N: No, not measured

III Wetting of liquid lead on patterned surfaces

III.1 Introduction

The dynamic wetting of silica-patterned iron surfaces by liquid lead was investigated using the techniques and materials presented in chapter II. Our aim was to better understand the effect of oxide size, distance between oxides and surface area fraction covered by oxides on wetting by a non-reactive metal.

Thus, for each lead droplet, the spreading diameter D, maximum height H_d and mean contact angle θ were measured as function of time. In order to compare the results obtained, the first two parameters are made dimensionless using the reference diameter $D_0 \approx 2.63 \text{ mm}$, the diameter of the liquid metal drop supposed to be spherical with the same weight as the metal ball. The mean contact angle is the average of the left and right contact angles. It should be noted that the difference between the left and right contact angles is neglected in this study because it is included in the measurement errors. The contact angle hysteresis was then deduced from these measurements (section II.3.6).

For each textured surface, at least two tests were performed under the same operating conditions, to ensure repeatability and consistency of measurements.

The experimental results obtained are presented and discussed in this chapter. First, the dynamic wetting of liquid lead on pure substrates (iron and silica) is presented and discussed (section III.2). These are the reference systems. Then, the dynamic wetting on the patterned surfaces is described and analysed to derive the main wetting parameters (section III.3).

Afterwards, it will presented a theoretical analysis of the influence of drop size and its position on the wetting. This analyse is then followed by an experimental study of the influence of pattern size and their distribution on the wetting.

At the end, the influence of silica covering yield on wetting is discussed. The influence is analysed on the final wetting state mainly characterized by the final contact angle and on the contact angle hysteresis.

III.2 Pure substrates

III.2.1 Pure iron

III.2.1.1.Dynamic spreading

General description

Figure III.2-1 shows the evolution of the dimensionless spreading diameter (a) and maximum height (b) of liquid lead on pure iron substrate as a function of spreading time and impact velocity. Figure III.2-2 shows the evolution of the mean contact angle as a function of spreading time (a) and spreading velocity (b). The three tests performed in this study are compared with the results from [1]. For each trial, the dispersion of the contact angles (standard deviation of the angles measured on the left and right) is indicated by means of error bars (Figure III.2-2a).

As shown in the figures, our measurements are in good agreement with the results obtained by Zaïdi [1]. They are also in good agreement with the experimental results presented in the literature for the same system (liquid lead / iron) [93]–[97]. Furthermore, the three tests give similar results with some differences which will be described and explained in the following.

In fact, the spreading of the liquid lead drop on pure iron at 450°C can be divided into several stages.

At first, the drop diameter increases and reaches a maximum value D_{max} after a spreading time τ^* between 10 ms and 12 ms. During this phase, the drop advances with an almost constant contact angle of a mean value θ_i (around 45°). The drop maximum height decreases during this stage before stabilizing when the spreading diameter becomes close to the maximum spreading diameter.

In the second stage, the droplet diameter decreases to a minimum diameter after 20-27 ms. In the meantime, the maximum height of the droplet increases, and the contact angle decreases sharply before stabilizing at a mean value of θ_{dr} (around 30°, Table III.2-1). At this stage, the spreading diameter and maximum height obtained for the impact velocity V_0 of 0.73 m/s (red points) deviate from the other tests: the drop receding is slowed down, the maximum height does not increase as much, and the contact angle decreases again to the minimum contact angle. The same phenomenon was observed on patterned surfaces with low silica coverage and will be discussed later. In addition, for all tests, there is a dispersion of the left and right contact angle of more than 10° (Figure III.2-2a). This dispersion is due to the oscillations of the liquid lead drop when receding.

In the third stage of spreading, the droplet undergoes a series of advancing and receding, leading to oscillations of the spreading diameter, maximum height and contact angle. In this stage, a maximum contact angle of $\theta_{da} \sim 57^{\circ}$ is reached. These oscillations do not exist for the impact velocity of $V_0 = 0.73 \ m/s$. This can be explained by the triple line pinning during the receding step.

Then, after a spreading time t_{stab}^d of less than 60 ms, the contact diameter of the drop stabilizes. At the beginning of this last stage, the drop height oscillates and the drop contact angle varies slightly. The drop height oscillation (not clearly shown in Figure III.2-1b) will be explained in more detail in chapter IV. Later, after a spreading time t_{stab}^a of more than 100 ms, the oscillations of the maximum drop height are damped. The spreading diameter and the contact angle of the drop become constant at the mean value D_f and θ_f respectively. Table III.2-1 shows the wetting parameters obtained, namely the mean initial contact angle θ_i , the receding contact angle θ_{da} , the final contact angle θ_f , the stabilization times t_{stab}^d and t_{stab}^a , the initial spreading time τ^* , the dimensionless maximal spreading diameter D_{max}/D_0 and the final spreading diameter D_f/D_0 . The minimum receding (θ_r) and maximum advancing (θ_a) contact angles measured at zero velocity (Figure III.2-2b) are also shown in the table.

In addition, the mean values of the spreading diameter, height and contact angle of the lead drop on pure iron are shown in Figure III.2-1 and Figure III.2-2 (solid black lines). These average curves are obtained by simply taking at each spreading time the mean value of the parameters for the three experiments. The wetting parameters estimated from these average curves are given in Table III.2-1. Subsequently, the average curves of liquid lead on pure iron will be used as a reference for the wetting on patterned surfaces.

The standard deviations related to the dispersion of the left and right contact angles are shown in Figure III.2-1. This standard deviation is often less than the measurement uncertainties that can be seen from one test to another. Thus, for greater clarity in the figures, dispersions related to differences in the left and right contact angles will not be displayed in the next graphs. Only the average value of the contact angle will be plotted for each test.

Table III.2-1: Wetting parameters of liquid lead spreading on pure iron.

V ₀	$ heta_i$	θ_{dr}	θ_{da}	$ heta_f$	t^d_{stab}	t^a_{stab}	$ au^*$	D _{max}	D_f	θ_r	θ_a
(m/s)	(°)	(°)	(°)	(°)	(ms)	(ms)	(ms)	D_0	D_0	(°)	(°)
0.75	39±6	31±3	60±3	52±1	66	100	11	3.71	1.81	46	57
0.73	48±6	30±4	50±4	55±3	48	100	9	3.44	1.62	44	56
0.60	50±7	30±3	62±2	55±1	50	100	10	3.19	1.63	52	59
Mean	45±6	30±3	57±3	54±1	55±2	100	10	3.44±	1.69±	47±3	57±2
0.69								0.18	0.08		
±0.08											
0.50	50±2	38±2	56±2	50±1	57±2	100	13±1	3.05	1.75	45±5	55±5
[1]						±10					



Chapter III: Wetting of liquid lead on patterned surfaces



Figure III.2-1: Dynamic wetting of lead on pure iron as function of spreading time and droplet impact velocity: (a) Dimensionless spreading diameter, (b) dimensionless droplet height.





Figure III.2-2: Mean dynamic contact angle of liquid lead on pure iron as function of (a) spreading time and (b) spreading velocity for different impact velocities. The errors described in (a) are the standard deviations estimated from the left and right contact angles.

Non-reactive wetting

The difference between the initial θ_i and the final θ_f contact angles is very small (less than 7°C) (Figure III.2-2 and Table III.2-1). This difference is in the same order as the measurement error of the contact angle in our experiments. This shows and confirms that there is no change in the chemical nature of the interface during spreading, i.e., the iron / lead system is not reactive (see section II.1.1).

Influence of the impact velocity

In our experiments, the weight of lead shot was kept constant at around 100 mg, then the kinetic energy depends only on the impact velocity V_0 . The latter varies from 0.60 to 0.75 m/s in pure iron experiments. This impact velocity is consistent with the maximum spreading diameter D_{max} reached at the spreading time τ^* : the higher the velocity, the larger the spreading diameter (Figure III.2-1a). After this first spreading phase, the impact velocity has a very small influence

on the parameters obtained, more particularly on the final spreading diameter D_f and the final contact angle θ_f .

Contact angle hysteresis

Figure III.2-2b shows the evolution of the mean contact angle as a function of spreading velocity U. The receding (θ_r) and advancing contact angle (θ_a) are respectively the minimum and maximum contact angle at zero spreading velocity (chosen here in the interval [-0.02 m/s, 0.02 m/s]). The measured contact angle hysteresis is given in θr) and maximum advancing (θ_a) contact angles measured at zero velocity (Figure III.2-2b) are also shown in the table.

In addition, the mean values of the spreading diameter, height and contact angle of the lead drop on pure iron are shown in Figure III.2-1 and Figure III.2-2 (solid black lines). These average curves are obtained by simply taking at each spreading time the mean value of the parameters for the three experiments. The wetting parameters estimated from these average curves are given in Table III.2-1. Subsequently, the average curves of liquid lead on pure iron will be used as a reference for the wetting on patterned surfaces.

The standard deviations related to the dispersion of the left and right contact angles are shown in Figure III.2-1. This standard deviation is often less than the measurement uncertainties that can be seen from one test to another. Thus, for greater clarity in the figures, dispersions related to differences in the left and right contact angles will not be displayed in the next graphs. Only the average value of the contact angle will be plotted for each test.

Table III.2-1 for each impact velocity. The hysteresis of about 10° obtained on pure iron is low and consistent with the results found in the literature [1]–[6]. The contact angle hysteresis is related to the presence of physical or chemical defects on the surface. In our experiments, after annealing at high temperature, the iron surface is facetted and slightly oxidized, with oxide particles of about a few nm in diameter (Figure III.2-3). The average roughness is less than 6 nm and its effect is negligible on wetting. The grain-boundary grooves formed do not cause any distortion of the triple line². Finally, the low presence of defects on pure iron samples after annealing explains the low hysteresis obtained.

²The roughness parameters were measured by means of atomic force microscopy (AFM *Digital Instruments Nanoscope IIIa*): the average roughness R_a defined as the average of the absolute value of the height of the points measured on the surface compared to the average plane was about 2 nm. In addition, the maximum roughness



Figure III.2-3: Iron surface after annealing at 850°C.

III.2.1.2.Droplet shape after solidification

Due to the pinning effects on pure iron during spreading, the triple line of liquid lead can deform and the contact angle can vary from one point to another on the triple contact line. The shape of the solidified lead drops was analysed from a lateral and a top view.

Lateral view

The solidified drop shape for the three tests performed on pure iron was reconstructed from the lateral view, using the technique presented in section II.4.1. This gives the dimensionless spreading diameter and contact angle around the periphery of the triple line (Figure III.2-4). The triple line is not perfectly circular, unlike what one would expect for a pure substrate. There is therefore a dispersion of the spreading diameter and contact angles due to surface defects (the

 R_{max} corresponding to the difference in height between the highest point and the lowest point of the annealed iron surface was around 200 nm [93].

triple line can be pinned by these defects when moving) and possibly drop deposition conditions. It is the measurement error related to our experimental conditions.

The maximum, maximum and mean values of both contact diameter $(D_{max}^l, D_{min}^l, D_m^l)$ and contact angle $(\theta_{max}^l, \theta_{min}^l, \theta_m^l)$ can then be determined (Table III.2-2). The final spreading diameter (D_f) and contact angle (θ_f) measured at high temperature are between the maximum and minimum values obtained in lateral view, in the experimental errors.

Impact velocity	D_{max}^l	D_{min}^l	D_m^l	D_f	θ_{max}^{l}	θ_{min}^{l}	$ heta_m^{l}$	$ heta_f$
<i>V</i> ₀ (m/s)	D_0	D_0	D_0	D_0	(°)	(°)	(°)	(°)
0.75	1.89	1.64	1.75±0.07	1.81	53	35	41±3	52
0.73	1.90	1.48	1.66±0.14	1.62	61	33	46±7	55
0.60	1.66	1.46	1.58±0.05	1.63	60	47	52±4	56

Table III.2-2: Main parameters of the solidified lead drop on pure iron from the lateral views.



Figure III.2-4: Lateral view of the solidified lead drops on pure iron. (a) Dimensionless spreading diameter, (b) drop contact angle as a function of angle of view.

Top view

If the lateral view gives details on the contact angle around the drop perimeter, a top view is more interesting for detailed characterizations of the drop surface contact. For that, the shape of the triple contact line was extracted by image analysis from the top view (section II.4.2). The algorithms presented in section II.4.2.1 were used to calculate the circularity criterion τ_c and

the corresponding optimal circle of diameter D_{opt}^{t} . The main results are summarized in Table III.2-3, i.e., the maximum and minimum Feret diameters $(D_{max}^{t}, D_{min}^{t})$ of the triple contact line, the diameter of the optimal circle, the final spreading diameter measured at high temperature D_{f} and the circularity criterion τ_{c} .

First of all, there is consistency between the two characterization techniques of the drop shape. The small differences between the spreading diameter results obtained in lateral and top views (Table III.2-2 and Table III.2-3) are due to measurement errors associated with both techniques. In fact, the maximum difference in diameter measurement obtained from the two views 0.07 $\left(\frac{D_{min}^{t}}{D_{0}} - \frac{D_{min}^{L}}{D_{0}}\right)$, for $V_{0} = 0.60 \text{ m/s}$) is in the measurement errors of about ±0.04 for both views.

Figure III.2-5 shows the shape of the surface contact of the lead drop and compares it to the optimal circle for the three tests performed on pure iron. The shape of the surface contact obtained for both tests with an impact velocity $V_0 = 0.60 \text{ } m/s$ and $V_0 = 0.75 \text{ } m/s$ is quite well described by a circle, with a circularity criterion of less than 0.1. With regard to the impact velocity V_0 of 0.73 m/s (red dots, Figure III.2-1, Figure III.2-2 and Figure III.2-4), the shape of the triple line differs slightly from the other tests: the triple contact line is further from the shape of a circle, with a circularity criterion of about 0.2. This can be explained by the fact that the triple line was pinned during its receding (Figure III.2-1).

One of the main results here is that the triple line can be deformed by pinning effects, even in the case of pure iron. In this case, the circularity criterion can be as high as 0.2. Therefore, for patterned surfaces, the values of circularity criterion less than 0.2 cannot be explained by the presence of silica pillars on iron.



Figure III.2-5: Shape of the triple line obtained for the solidified lead droplets on pure iron as function of droplet impact velocity. a) Experimental shape obtained from top view, b) Triple line contour and optimal circle, c) Difference between the optimal circle an

Table III.2-3: Parameters characterizing the triple line of the solidified lead droplet on pure iron from a top view.

Impact velocity	D_{max}^t	D_{min}^t	D_{opt}^t	D_f	τ
<i>V</i> ₀ (m/s)	D_0	D_0	D_0	$\overline{D_0}$	ι _c
0.75	1.87	1.61	1.69	1.81	0.07
0.73	1.90	1.46	1.62	1.62	0.17
0.60	1.67	1.53	1.60	1.63	0.06

The investigation of the wetting of pure iron by liquid lead will be a reference system in the work presented here. The tests performed on the silica patterned iron will be compared to this reference system. We also conducted experiments on pure silica (actually thin layer of silica deposited on pure iron, section II.1.1.1)) as another reference.

[123]

III.2.2 Pure silica

III.2.2.1.Dynamic spreading

Figure III.2-6 shows the evolution of the dimensionless spreading diameter (a) and maximum height (b) of liquid lead on pure silica substrate as a function of spreading time and impact velocity. The evolution of the mean contact angle as a function of spreading time (a) and spreading velocity (b) is also shown in Figure III.2-7. The two tests performed for this system are compared with the results from [1]. The wetting parameters obtained are given in Table Table III.2-4 (with the same notation as above for the case of pure iron).

The dynamic wetting of lead on pure silica observed is consistent with the results published in the literature [1], [89], [98], [99] (Figure III.2-6 and Figure III.2-7). As in these previous experiments, the spreading of the liquid lead drop on silica can be divided into several steps as observed on pure iron.

First, the droplet spreading diameter increases and reaches a maximum value D_{max} after a spreading time τ^* of about 10 ms and the drop advances with an almost constant contact angle (θ_i). The maximum droplet height decreases during the first ms and then remains constant.

In the second stage, the drop recedes. The maximum height increases to a maximal value and the contact angle decreases sharply before increasing. At the end of this step, the droplet bounces back ($V_0 = 0.60$ m/s and [1]). The rebound is due to the high initial kinetic energy of the droplet. The forced wetting leads to an initial contact angle much lower than the contact angle obtained at thermodynamic equilibrium (about 135°). When the triple line recedes, the surface energy at the maximum diameter is then mainly converted into kinetic energy. This explains why the dewetting step is followed by a rebound. It should be noted that the rebound was not observed in the second test ($V_0 = 0.86$ m/s, red marks in Figure III.2-6). In this case, the maximum spreading diameter is smaller. This implies that the surface energy stored in the deformation of the liquid surface at this point is smaller and then the kinetic energy recovered during receding does not allow a rebound. This is a surprising result because the impact velocity is higher. This means that the energy dissipation is higher than in the first case (the reason is not understood, perhaps small defects in the silica layer that hold the drop in motion).

In the third stage of spreading, the droplet undergoes a series of advancing and receding, leading to oscillations of the spreading diameter, maximum height and contact angle. These oscillations

last much longer than on pure iron. The dissipation of kinetic energy takes longer on less wettable surfaces because the triple line slides more freely on the substrate. At the end of the third stage, the spreading diameter, maximum height and contact angle of the drop are nearly constant at the mean values D_f and θ_f respectively, after a spreading time t_{stab}^a of more than 500 ms.

V ₀	$ heta_i$	θ_{dr}	θ_{da}	$ heta_f$	t^d_{stab}	t^a_{stab}	$ au^*$	D _{max}	D_f	$ heta_r$	θ_a
(m/s)	(°)	(°)	(°)	(°)	(ms)	(ms)	(ms)	D_0	$\overline{D_0}$	(°)	(°)
0.60	121	85	149	134	400	700	10	2.75	0.77	122	145
	±4	±5	±8	±2							
0.86	118	100	155	137	200	600	9	2.39	0.79	124	150
	±8	±б	±б	±3							
Mean:	120	93	152	136	300	650	9	2.57	0.78	123	147
0.73	±б	±5	±7	±2	±100	±50	±1	±0.18	±0.01	±1	±3
±0.13											
0.54	147	112	129	129	150	750	7	1.70	0.88	116	144
[1]	±2	±4	±6	±3	±5	±10				±3	±3

Table III.2-4: Parameters of wetting dynamics of liquid lead on pure silica.







Figure III.2-6: Dynamic wetting of lead on pure silica as function of spreading time and initial velocity: (a) Dimensionless spreading diameter, (b) dimensionless drop height.



Figure III.2-7: Mean contact angle of liquid lead on pure silica as function of (a) spreading time and (b) spreading velocity for different impact velocities.

[127]

Non-reactive wetting

The difference between the initial θ_i and the final θ_f contact angles in Table III.2-4 is small, confirming that the iron / silica system is not reactive [14], [93], [100].

Contact angle hysteresis

Figure III.2-7b shows the evolution of the mean contact angle as a function of spreading velocity U. The contact angle hysteresis is measured at zero spreading velocity (chosen here in the interval [-0.02 m/s, 0.02 m/s]). The hysteresis of about 20° is in agreement with the results of the literature [14], [15]. The contact angle hysteresis is related to the presence of physical or chemical defects on the surface.

I.1.1. Droplet shape after solidification

At the end of the experiment, the solidified drop on pure silica was also analysed. However, since pure silica is not wetted by liquid lead (contact angle greater than 130°), only the drop shape obtained from a lateral view is relevant.

The shape of the solidified drop for both tests was reconstructed from the lateral view, using the technique presented in section II.4.1. Figure III.2-4 shows the dimensionless contact diameter and contact angle of the solidified drop depending on the angle of view α_{ν} . As for pure iron, the main dimensions and contact angles of the solidified drop are given in Table III.2-5. There is a good agreement between the measured values at high temperature and on the solidified drop.

In both cases, the surface contact of the drop on pure silica is circular. The dispersion on spreading diameter and contact angle is the measurement error.

Impact velocity V_0 (m/s)	$\frac{D_{max}^l}{D_0}$	$\frac{D_{min}^l}{D_0}$	$\frac{D_m^l}{D_0}$	$\frac{D_f}{D_0}$	$ heta_{max}^l$ (°)	$ heta_{min}^l$ (°)	$ heta_m^l$ (°)	$ heta_f$ (°)
0.60	0.75	0.67	0.70±0.02	0.77	143	132	137±3	134
0.86	0.77	0.68	0.73±0.03	0.79	143	130	136±4	137

Table III.2-5: Main parameters of the solidified lead drop on pure silica from a lateral view.



Chapter III: Wetting of liquid lead on patterned surfaces

Figure III.2-8: Lateral view of solidified lead drop on pure silica. (a) Dimensionless spreading diameter, (b) contact angle as a function of angle of view.

III.2.3 <u>Recapitulation</u>

Before investigating the wetting of liquid lead on patterned surfaces, we analysed the wetting of reference surfaces: pure iron and silica.

The dynamic wetting of liquid lead on pure substrates was consistent with the experiments presented in the literature for spreading diameter, contact angle and contact angle hysteresis. Experiments with impact velocities ranging from 0.6 m/s to 0.75 m/s were carried out on pure iron (silica surface fraction close to zero). Note that this difference in impact velocity is not well controlled with our device, since the pressure exerted for dropping is poorly controlled. From the experiments, an average evolution of spreading diameters, drop heights and contact angles as a function of time was calculated, which would correspond to the case of an average impact velocity of $V0 = 0.69 \pm 0.08 m/s$. It will be our reference for wetting on pure iron. Similarly, the average evolution of the above-mentioned parameters on pure silica (100% of silica surface fraction) will be our reference for pure silica. The average impact velocity is $V_0 = 0.71 \pm 0.15 \text{ m/s}$ for this substrate.

The results confirmed that the dynamic wetting of liquid lead on pure iron and pure silica is a non-reactive wetting, as the initial and final contact angles are of the same order of magnitude. At zero spreading velocity, a contact angle hysteresis of about 10° was measured on pure iron and about 20° on pure silica.

In addition, we analysed the shape of the solidified drop in lateral view (on pure iron and pure silica) and in top view (only on pure iron). The triple line is generally not a perfect circle on pure iron, with a circularity criterion up to 0.17. This is due to pinning effects of liquid lead on pure iron with a contact angle of $46\pm7^{\circ}$. On pure silica, an almost circular shape of the solidified drop was obtained, because liquid lead does not wet pure silica (contact angle of $135^{\circ}\pm5$).

In the following, pure iron and pure silica are used as references with silica surface fractions of 0 and 1. The wetting of patterned surfaces (silica surface fraction from 3% to 70%) will be compared to that of pure substrates at high and low temperatures.

III.3 Dynamic spreading on patterned surfaces

III.3.1 General description

Figure III.3-1 and Figure III.3-2 show the evolution of the dimensionless spreading diameter, maximum height and mean contact angle of liquid lead on textured surfaces compared to pure substrates. The impact velocity is almost identical, about 0.70 m/s (the difference is due to the difficulty of controlling this impact velocity). The patterned surfaces considered have the same length of the side of the silica pillars ($d = 20 \ \mu m$) but a different distance between them and therefore a different silica surface fraction: 64% for the {20; 5} samples, 25% for the {20; 20} samples and 3% for the {20; 100} samples. The results presented in the figures are average behaviours obtained from the two tests performed on each patterned surface (see section III.3.2 for more details on each test,). For reasons of clarity, the errors are not shown in these figures.

The dynamic wetting shown in Figure III.3-1 and Figure III.3-2 is similar during the first milliseconds for all samples. After impact, the drop advances and reaches the maximum spreading diameter D_{max} after a spreading time between $\tau^* = 8 \text{ ms to } \tau^* = 10 \text{ ms}$ (Figure III.3-1a). The maximum spreading diameter increases as the silica surface fraction increases. The effect of surface wettability on the maximum spreading diameter will be discussed in more detail in chapter IV. As the drop advances, its maximum height decreases rapidly before stabilizing (Figure III.3-1b). At the same time, the drop contact angle increases slightly (Figure III.3-2a). The mean initial contact angle θ_i obtained during this first step increases as the silica surface fraction increases.

In the second stage, differences are observed between patterned samples during drop receding.

On the {20; 5} sample with a high silica surface fraction (64%), the dynamic wetting is identical to that on pure silica: the drop recedes easily, the spreading diameter and the contact angle decrease rapidly before increasing. The large dispersion of the contact angle during this step is due to the oscillations of the drop caused by the dissipation of the initial kinetic energy. The second step is then followed by damped advancing and receding cycles.

On {20; 20} and {20; 100} samples (with low and moderate silica area fractions), the receding of the liquid lead drops is different. Indeed, the triple line is pinned during receding at 16 ms (i.e. the spreading diameter is fixed) and the maximum height does not increase. The same results were obtained in one of the pure iron tests (Figure III.2-1a, $V_0 = 0.73$ m/s). Regardless

of the silica surface fraction, the dynamic contact angles on these two samples and on pure iron are very close (Figure III.3-2) due to this pinning effect. At the end of this stage, the drop does not have enough energy to advance again, it stabilizes and rapidly reaches its final stage.

The pinning effect of the liquid lead drop on the part occupied by metallic iron can lead to its division into two smaller droplets ({20; 100} sample, full and empty black circles, Figure III.3-1 and Figure III.3-2). Our results suggest that the pinning effect of liquid drops occurs on patterned samples with low and moderate silica area fractions: in 6 out of 7 tests or 68% tests on surfaces with low silica area fraction (3-4%), 3 out of 7 tests or 43% on surfaces with moderate silica area fraction (25%) and only 1 out of 8 tests or 13% tests on surfaces with high silica area fraction (more than 64%). This phenomenon will be more analysed in section III.4.





Figure III.3-1: Dynamic wetting of liquid lead on pure substrates and patterned surfaces with different silica surface fractions: (a) Dimensionless spreading diameter, (b) Maximum dimensionless droplet height.







Figure III.3-2: Mean dynamic contact angle of liquid lead on pure substrates and patterned surfaces with different silica surface fractions as a function of (a) spreading time and (b) spreading velocity.

III.3.2 <u>Main wetting parameters</u>

The wetting parameters obtained for each trial in the measurement direction d1 or d2 are given in Table III.3-1, with the same notations as in Table III.2-1: the mean initial contact angle θ_i , the first receding contact angle θ_{dr} , the first advancing contact angle θ_{da} , the final contact angle θ_f , the stabilization time of spreading diameter (t_{stab}^d) and contact angle (t_{stab}^a) , the initial spreading time τ^* , the dimensionless maximum spreading diameter D_{max}/D_0 and final spreading diameter. The minimum receding (θ_r) and maximum advancing (θ_a) contact angles measured at zero velocity are also shown in Table III.3-1 (see section II.3.6, for more information on the measurement of contact angle hysteresis).

In most tests, there is small difference (less than 10°) between the initial and final contact angles, considering the measurement errors of contact angle. This result confirms the wetting of the systems studied is non-reactive.

Subsequently, these wetting parameters will be analysed to infer the characteristics and mechanisms of wetting of silica-iron surfaces by liquid lead.

V ₀	d1 or	θ_i	θ_{dr}	θ_{da}	θ_{f}	t ^d _{stab}	t^a_{stab}	$ au^*$	D _{max}	D _f	θ_r	θ_a			
(m/s)	d2	(°)	(°)	(°)	(°)	(ms)	(ms)	(ms)	D ₀	$\overline{D_0}$	(°)	(°)			
	Pure iron ($f_{si0_2} = 0\%$)														
0.69	-	45±6	30±3	57±3	54±1	55±2	100	10	3.44	1.69	47	57			
				<u>{5</u>	; <u>20</u> }, ($f_{sio_2} =$	4 %)								
0.81	d1	71±3	38±4	63±6	56±1	111	100	10	3.60	1.67	39	70			
0.91	d2	30±3	22±2	-	48±1	37	71	8	3.82	-	21	50			
	$\underline{\{20;100\}}, (f_{Si0_2} = 3\%)$														
0.78	d1	73±8	44±2	-	63±1	55	55	9	3.48	-	47	72			
0.83	d2	60±2	42±2	60±3	58±1	36	55	9	3.75	-	48	63			
				{100); 500},	(<i>fsio</i> ₂	= 3 %)								
0.70	d1	42±5	26±4	59±4	59±2	58	100	10	3.55	1.47	39	63			
0.48	d2	65±6	50±4	89±5	69±1	51	91	8	2.50	1.47	61	101			
0.70	d1	53±5	40±6	51±3	56±1	91	91	10	3.59	-	48	57			
	$\{5;5\}, (f_{SiO_2} = 25\%)$														
0.69	d1	53±5	36±6	76±4	61±2	55	100	9	2.86	1.56	56	73			
				{20	; <u>20</u> }, (j	$f_{SiO_2} =$	25%)								
0.90	d1	61±8	37±5	50±5	55±1	53	100	9	3.24	1.59	27	70			
0.71	d2	59±3	37±4	-	55±1	45	100	10	2.86	1.29	30	57			
				<u>{100</u>	; 100},	(<i>fsio</i> ₂ =	= 25%))							
0.75	d1	66±6	47±5	88±6	69±3	34	100	8	3.05	1.47	56	97			
0.32	d2	39±2	31±6	58±3	55±1	35	100	13	2.60	1.11	35	61			
				{500	; 500},	(<i>f</i> _{si02} =	= 25%))							
0.54	d1	65±3	35±4	84±6	67±1	63	100	8	2.68	1.48	53	86			
0.59	d2	54 ±11	36±5	64±5	70±5	45	100	11	3.02	1.47	49	68			
				<u>{20</u>); <u>5</u> }, (f	$s_{i0_2} =$	64%)								
0.72	d1	83±5	66±5	105	99±1	101	300	8	2.33	1.01	80	109			

Table III.3-1: Wetting parameters of liquid lead on patterned surfaces.

Chapter III: V	Wetting	of lic	juid	lead	on	patterned	surfaces
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				±5								
0.70	d2	74±6	61±5	114 ±4	99±2	101	300	7	2.61	1.09	89	114
$\underline{\{100; 20\}}, (f_{SiO_2} = 69\%)$												
0.76	d1	76±6	54±4	111 ±4	108 ±1	101	300	8	2.42	1.12	77	111
0.79	d2	75±7	62±4	121± 6	125 ±3	110	300	6	2.74	0.79	95	139
$\{500; 100\}, (f_{SiO_2} = 69\%)$												
0.66	d1	98±4	59±4	112 ±4	104 ±2	94	300	7	2.40	1.00	70	118
0.39	d2	88 ±10	62±4	106 ±6	91±2	92	300	8	1.98	1.22	73	111
Pure silica ($f_{SiO_2} = 100\%$)												
0.71	-	120 ±6	93±5	152 ±7	136 ±2	300 ±100	650 ±50	9 ±1	2.57 ±0.18	0.78 ±0.01	123 ±1	147 ±3

III.4 Stick – slip motion

When the fraction of the surface occupied by silica is low (3%) and moderate (25%), the triple line advances by stick-slip motions (section III.4.1). During its receding, the drop is strongly pinned by the parts of the surface occupied by pure iron: sticking phase (fixed contact diameter of the drop). Then when it is favourable, the drop continues its receding: slipping phase. As a result, the triple contact line of the drop is deformed and surrounds the silica pillars to remain preferably on pure iron, which leads to different solidified drop shape (sections III.4.2).

III.4.1 Evidence of stick-slip motion during spreading

Figure III.4-1a shows the change in the spreading diameter over time for liquid lead droplets on patterned surfaces with low silica area fraction (4%) together with the mean spreading on pure iron. The stick-slip motion of the triple line is highlighted for three patterned substrates at approximately the same spreading times. For all the three tests, at the first seconds of spreading, the lead drop on the patterned substrates behaves like on pure iron. Then, the droplet spreading diameter deviates from the case of pure iron: the spreading diameter on patterned substrates

remains constant for a few ms (sticking phase). This is because the triple line is pinned by the metallic iron parts of the substrate during its receding. The triple line can then move back (slipping phase) before being pinned again at around 26 ms. In a final step, the drop moves back again and can either reach its final spreading diameter ({5; 20} and {100; 500} black circles) or be divided into two or more droplets ({100; 500} red circles).

The mean contact angle is also shown in Figure III.4-1b. The evolution of this contact angle is very similar for all the three textures and very close to the case of pure iron. On the patterned substrates, when the drop remains pinned to a constant diameter as it recedes, the contact angle decreases for the first diameter level and increases slightly for the second level. This could be explained by an overlapping of the receding movement of the drop triple line and oscillations of the whole drop.

In Table III.4-1, the behaviour of the drop (followed according to the direction d1 or d2) when it recedes is summarized for all our tests: *p*. is used if the drop is pinned and the *spl*. if the drop is divided into several drops. In the case the drop splits, the number in brackets indicates the number of the small droplets obtained.




Figure III.4-1: Stick slip motion of liquid lead on patterned samples with low silica area fraction: (a) Dimensionless spreading diameter, (b) Mean dynamic contact angle.

Table III.4-1: Summary of the stick-slip motion on silica patterned surfaces. Measurement direction is marked with d1 (direction 1) and d2 (direction 2). Pinning effects were observed on the experiment with the mark p. and drop splitting by the mark spl...

Pure iron		n	{5	; 20}	{20; 100}		{	{100; 500}		
($f_{SiO_2} = 0$	9%)	$(f_{Si0_2} = 4\%)$		$(f_{SiO_2} = 3\%)$		(f .	$(f_{SiO_2} = 4\%)$		
-	-	-	d1	d2	d1	d2	d1	d2	d 1	
0.75	0.73	0.60	0.81	0.91	0.78	0.83 m/s	0.70	0.48	0.70	
m/s	m/s	m/s	m/s	m/s	m/s	0.05 11/8	m/s	m/s	m/s	
-	р.	-	р.	<i>p</i> .	р.	<i>p. p.</i>		-	р.	
-	-	-	-	<i>spl.(4)</i>	spl.(2)	<i>spl.(2)</i>	-	-	<i>spl.(2)</i>	
	{5;5}		{20); 20}	{100	; 100}	{	500; 50)0}	
()	$S_{siO_2} = 2!$	5%)	(<i>fsio</i> ₂	= 25%)	$(f_{sio_2}$	= 25%)	$(f_{sio_2} = 25\%)$		25%)	
	d1		d1	d2	d1	d2	d1		d2	

0.69	0.9	0 0.71	0.75	0.32 m/s	0.54	0.59
m/s	m/s	s m/s	m/s		m/s	m/s
-	<i>p</i> .	р.	-	р.	-	-
{20; 5}	{	100; 20}	{500; 100}		Pure silica	
$(f_{SiO_2} = 64\%)$	(f _{Si}	$o_2 = 69\%$	9%) $(f_{SiO_2} = 69\%)$		(f _{sic}	₀₂ = 100 %)
d1 d	2 d	1 d2	d1	d2	-	-
0.72 0.7	0.7	6 0.79	0.66	0 39 m/s	0.55	0.86
m/s m	s m/s	s m/s	m/s	0.39 m/s		m/s
p	-	-	-	-	-	-

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III.4.1.1.Influence of silica patterns

As shown in Table III.4-1, the drop remains pinned when it recedes in almost all cases (6 out of 7 tests) when the silica surface fraction is low (3-4%). The drop is divided into several droplets in more than half of the tests (4 out of 7 tests). As mentioned in section III.2.1.1, the drop can also remain pinned in the case of the pure iron substrates but it is rarer (1 test out of 3). This shows that silica pillars are involved in the pinning and division of the drop. In fact, on these patterned substrates, stick-slip motion is favourable due to the large distance between patterns compared to the pattern size. With regard to the moderate silica surface fraction (25%), the drop can remain pinned during receding (3 out of 7 tests) but never splits into several droplets. When the silica surface fraction is high (64%), the drop almost never gets pinned during receding (1 trial out of 8).

III.4.1.2. Influence of spreading direction

Table III.4-1 shows the stick-slip motion on patterned surfaces depending on the measurement direction (d1 or d2). On patterned surfaces with silica area fraction of 3% or 25%, eight (8) experiments were done in the direction d1 and six (6) in the direction d2. Stick-slip motion was observed for five (5) experiments in direction d1 and for four (4) experiments in the direction d2. Stick-slip motion leading to drop splitting was observed on two experiments in both directions. Then, these results do not show any influence of the measurement direction on the stick-slip phenomenon or on the drop division.

III.4.1.3. Drop splitting during the sticking phase

During the sticking phase, the diameter of the drop is nearly constant but the interface liquidgas oscillates (Figure III.4-2). This oscillation may lead to the splitting of the drop into two or several droplets, when energetic condition is satisfied (section IV.6).



Figure III.4-2: Example of stick slip motion leading to drop splitting: the case of $\{100; 500\}$ sample with V₀=0.70 m/s.

As result, the triple contact line of the small droplets were observed to rest mainly on pure iron avoiding silica patterns (Figure III.4-4).



Figure III.4-3: SEM images of lead droplet shape and TCL position on {100; 500} patterned surfaces.

III.4.2 <u>The shape of the triple contact line</u>

Due to the adhesion of the drop to the metallic iron parts of the surface, the dynamic contact angle is close to that obtained on pure iron. Consequently, the stick-slip motion can influence the solidified drop shape. In the case of the undivided drops, we used two approaches: first, a study of the macroscopic shape of the drop through a top view, and then, the determination of the position of the triple line of the drop in relation to the silica patterns.

III.4.2.1. Circularity criterion

The shape of the triple line has been reconstructed from the top view (section II.4.2.1), for patterned surfaces wetted by liquid lead (contact angle less than 90°) and when the drop is not divided during spreading. The numerical procedure makes it possible to calculate the maximum diameter (D_{max}^t) , minimum diameter (D_{min}^t) , optimal diameter (D_{opt}^t) and circularity criterion (τ_c) of the reconstructed drop shape (Table III.4-2).

In all cases, the circularity criterion obtained is less than 0.17, which corresponds to the maximum circularity criterion obtained for pure iron (Table III.2-3). These results show that the effect of silica patterns on the macroscopic shape of the triple line is of the same order of magnitude as the effect of other defects that may be present on surfaces (grain boundaries, metallic steps, nanometric oxide particles).

The circularity criterion alone is not sufficient to predict whether the droplet has been trapped during its spreading. However the majority of droplets that were pinned during receding are characterized by a circularity criterion greater than 0.1 (5 out of 6 trials including pure iron, or 83%) while the majority of droplets that were not pinned during receding are characterized by a circularity criterion less than 0.1 (5 out of 7 trials including iron, or 71%). The circularity criterion is less than 0.05 if the triple line is less retained by the metallic iron parts. This shows that the stick-slip motion effectively causes a greater deformation of the drop shape.

The circularity criterion provides macroscopic information on the drop shape but not on the deformation of the triple contact line on patterned surfaces. It is then necessary to position the triple contact line in relation to the silica pillars.

Table III.4-2: Parameters characterizing the triple line of the undivided solidified lead droplet on patterned surfaces from a top view. p. indicates the stick-slip motion and spl. the split drops.

$V_0 \left(\frac{m}{s}\right);$ $\frac{d1}{d2}$	p., spl.	$\frac{D_{max}^t}{D_0}$	$\frac{D_{min}^t}{D_0}$	$\frac{D_{opt}^t}{D_0}$	$\frac{D_f}{D_0}$	$ au_c$
		{5;	20}, $(f_{SiO_2} =$: 4%)		
0.81; d1	р.	1.65	1.39	1.55	1.62	0.12

$\{100; 500\}, (f_{SiO_2} = 3\%)$											
0.7; d1	р.	1.82	1.50	1.63	1.49	0.12					
0.48; d2	-	1.44	1.37	1.40	1.46	0.03					
	$\{5; 5\}, (f_{SiO_2} = 25\%)$										
0.69; d1	-	1.63	1.60	1.61	1.56	0.02					
		{20;	20}, $(f_{SiO_2} =$	25%)							
0.90; d1	р.	1.74	1.38	1.55	1.59	0.17					
0.71; d2	р.	1.67	1.29	1.43	1.29	0.17					
		{100;	100}, $(f_{SiO_2} =$	= 25%)							
0.75; d1	-	1.40	1.37	1.38	1.47	0.04					
0.32; d2	р.	1.66	1.55	1.60	1.71	0.05					
		{500;	500 , $(f_{Si0_2} =$	= 25%)							
0.54; d1	-	1.44	1.36	1.39	1.48	0.11					
0.59; d2	-	1.46	1.39	1.41	1.47	0.13					

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III.4.2.2. Lead drop position with respect to silica patterns

The effect of the silica pillars can be observed with the triple contact line deformation. The triple line (blue line) and the contact surface of the corresponding optimal circle (light blue) are positioned with respect to the texture patterns (red squares). We can only conduct this analysis on textures with sufficiently large patterns (more than $100 \mu m$).

For example, the position of lead drops at the end of spreading on {100; 500} and {100; 100} samples is shown in Figure III.4-4. As indicated in Table III.4-2 and Table III.4-3, we chose to represent two trials for each texture: the drop underwent stick-slip movements for the first trial (Figure III.4-4.a and Figure III.4-4.d) and did not undergo stick-slip movement for the second

(Figure III.4-4.b and Figure III.4-4.c). This choice makes it possible to compare the effect of the triple line pinning on its final shape.

Table III.4-3 shows the silica surface fraction $(f_{SiO_2})_{surf}$ and the silica linear fraction $(f_{SiO_2})_{TCL}$ at the triple contact line calculated using the precise position of the triple contact line. The corresponding equilibrium contact angles θ_{surf} and θ_{tcl} calculated with Eqs. (I.2.4) and (I.2.6) are also given. These calculations were made for both the solidified drop and its optimal circle. The values in brackets indicate the results obtained with the optimal circle.

In all cases, whether or not the triple line is pinned during receding, the surface fraction of silica under the drop remains constant and equal to the average surface fraction of silica: ~ 0.03 for $\{100; 500\}$ samples and ~ 0.25 for $\{100; 100\}$ samples. This result is not surprising, as discussed in Section III.5.1, because at these pattern sizes and distances between patterns, the volume of the drop is large enough that these surface fractions do not change when the position of the TCL changes.

As far as concerned the silica linear fraction, two conclusions can be drawn about the real shapes of the triple line depending on whether they are compared to their optimal circle or whether they are compared with each other.

When the triple line is pinned during receding, the silica linear fraction at the triple line is lower for the real triple line than for the optimal circle only for {100; 500} sample (Figure III.4-4.a) $((f_{siO_2})_{tcl} = 0.005 \text{ against } 0.023)$. This difference does not exist for the {100; 100} sample because the deformation of the triple line is small and the comparison is therefore not relevant.

The result is more interesting by comparing the drops with each other according to whether they were retained or not during the receding. Indeed, the TCL of the drops that were retained by pure iron (indicated by p. in Table III.4-3) are mainly on pure iron compared to the one where the drops were not.



Figure III.4-4: TCL positioning of lead drop toward silica patterns on two different patterned surfaces: {100; 100} and {100; 500}. Pinning effect was observed for the images in a) and d).

Table III.4-3: Linear and area fraction of the reconstructed TCL of lead drop on patterned surfaces.

$V_0\left(\frac{m}{s}\right);$ $d1/d2$	Pinning, <i>p</i> .	$(f_{sio_2})_{surf}$	$(f_{sio_2})_{tcl}$	$ heta_{surf}(^{\circ})$	$ heta_{tcl}(^{\circ})$
	{	$[100; 500\}, (f_{SiO_2} =$	= 0.03)		

0.7		0.028	0.005	57	55
d1	р.	(0.028)	(0.023)	(57)	(57)
0.48		0.027	0.038	57	58
d2	-	(0.027)	(0.025)	(57)	(57)
	-	$\{100; 100\}, (f_{SiO_2} =$	= 0.25)		
0.75		0.253	0.286	75	77
d1	-	(0.251)	(0.190)	(74)	(70)
0.32		0.249	0.232	74	77
d2	p.	(0.251)	(0.219)	(74)	(70)

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III.4.3 <u>Recapitulation</u>

A liquid lead drop deposited on an iron surface covered with silica pillars remains pinned when it recedes, when the silica surface fraction is low (3-4%), and the drop can be divided into several droplets. With regard to the moderate silica surface fraction (25%), the drop can remain pinned during receding but never splits into several droplets (section III.4.1). The triple contact line of the drop is deformed and surrounds the silica pillars to remain preferably on pure iron (section III.4.2). We can therefore assume that the triple line remains pinned to metallic iron when it recedes.

On the other hand, silica pillars seems to be involved in the pinning and division of the drop. This point will be further investigated in energetic view in section IV.6.

III.5 Influence of spreading directions

III.5.1 Critical drop size

In sections I.1.6.4 and I.1.6.5, we have shown the influence of the size of the substrate defect on the shape of the drop contact line [14], [15], [22], [23]. Depending on the defect scale in relation to the drop size, different contact angles can be obtained. However, for a surface covered with defects whose distribution is isotropic [37], [39], [47]–[52], there is a critical drop

size (D_c) beyond which the contact angle becomes independent of the location of the drop triple contact line and the size of the drop contact area.

Critical spreading diameter

For the patterned surfaces studied here, simple calculations for the critical drop size are possible. And first, patterned surfaces with different square silica size and area fraction were reproduced as a simple image using MATLAB. Then for different theoretical drop size (considered as spherical) deposited on each patterned surface, the linear and area fractions of the drop on silica were calculated using techniques of image comparisons (developed under MATLAB).

To study the influence of the position of the triple line, five positions of the drop were considered as indicated in Figure III.5-1. The blue disk correspond to the contact surface between the drop and the patterned substrate. Its diameter is representative of the so-called spreading diameter D in our experiments.



Figure III.5-1: The five different positions (cases) of the drop centre toward patterns selected for calculations.

Figure III.5-2 shows triple contact line (*TCL*) fraction and contact area fraction on silica of the theoretical spherical drops deposited on patterned surfaces depending on the centre of the drops (indicates as $\langle\langle case \rangle\rangle$ in Figure III.5-2 and Figure III.5-1). Patterned surfaces with the same silica area fraction than our experimental study (3%, 25% and 70%) are considered. It should be noticed that, at a given silica area of patterned surfaces, results depend only on the ratio of the drop size (*D*) to the size of the patterns (*a* + *s*).

The figure also shows the influence of the position of the drop centre. Depending on the drop size and the position of its centre, linear fraction of the triple contact line on silica is different. A periodic variation of the linear fraction was obtained (Figure III.5-2.a). These variations of the linear fraction is another explanation of the origin of the contact angle hysteresis on the patterned surfaces due to its heterogeneity.





Figure III.5-2: TCL linear and surface fractions of silica under theoretical spherical drops (contact surface diameter D) placed on silica-patterned iron surfaces {a; s}. Three surface groups with different silica area fractions (3%, 25% and 70%) were tested. Each colour corresponds to a different position of the theoretical drop centre (Figure III.5-1).

However, the variation in the surface area fraction occupied by silica under the drop is smaller than the linear fraction of silica at the triple line. For small drops, this silica surface fraction varies greatly with the diameter of the drop / substrate contact surface and the position of its centre. For large drops, it tends towards the silica area fraction of the patterned surfaces (Figure III.5-2b). The critical value of the drop contact size is found to be around 5 (with calculation errors of area fraction of ± 0.005):

$$\frac{D_c}{a+s} = 5$$
 (III.5.1)

Then, the size of the drop contact surface must be equal to at least five times the pattern size (a + s) so that its position has no influence on wetting.

Comparison between experimental and critical spreading diameter

This criterion is calculated for all the textures studied here and compared to the dimensionless spreading diameter measured at 1 ms and at the end of the spreading in our experiments (Table III.5-1).

For the smallest pattern sizes, i.e. {5; 20}, {20; 100}, {5; 5}, {20; 20}, {100; 100}, {20; 5}, {100; 20}, the dimensionless spreading diameters are larger than the critical dimensionless diameter for any spreading time. We can then expect a limited influence of the direction of the triple line compared to the direction of the texture.

On the other hand, for the largest pattern sizes, i.e. {100; 500}, {500; 500}, {500; 100}, the initial and final spreading diameters are of the same order of magnitude as the critical dimensionless diameter, which could lead to differences in behaviour depending on the direction of spreading. These three cases will be discussed in more detail in section III.5.2.

Table III.5-1: Dimensionless critical drop size compared to dimensionless spreading diameter at 1 ms and at the end of spreading (D_f/D_0) .

$\{d;s\}$	Dc = 5.(d+s)	D_c / D_0	D / D ₀	D_f/D_0
	[µm]		(at 1 ms)	
{5; 20}	125	0.05	~ 0.7	~ 1.7
{20; 100}	600	0.23	1 – 1.3	-
{100; 500}	3000	1.15	0.8 – 1.2	~ 1.5
{5;5}	50	0.02	~ 0.5	~ 1.6
{20; 20}	200	0.08	1.1 – 1.2	~ 1.6
{100; 100}	1000	0.38	1.2 - 1.4	~ 1.1
{500; 500}	5000	1.92	~ 0.5	~ 1.5
{20; 5}	125	0.05	~ 0.8	~ 1.0
{100; 20}	600	0.23	~ 1.0	0.8 - 1.1
{500; 100}	3000	1.15	0.4 - 0.7	1.0 - 1.2

As an example of what happens when the drop is too small for the size of the patterns, we can look at the drop obtained on the the {500; 500} sample. The final drop diameter is $D_f = 1.48D_0 \sim 4 \text{ mm}$, then $\frac{D_c}{d+s} = 4 < 5$. In this case, the drop size is not sufficient for isotropic wetting. This result is in agreement with the deformed shape of the solidified drop obtained (Figure III.5-3).



Figure III.5-3: Anisotropic solidified lead drop on {500; 500} sample.

Theoretical error on the contact angle

This discussion is based on a calculation of the equilibrium contact angle estimated for any spreading diameter. Obviously, the reality is more complex since the contact angle is dynamic. The drop surface contact is often not circular and the TCL is tortuous even for the smallest pattern sizes due to stick-slip motion for instance (section III.4).

III.5.2 Influence of spreading direction

III.5.2.1.High temperature

At high temperature, wetting experiments were performed following two different directions for each patterned samples, direction d1 (parallel to the sides of the silica pillars) and direction d2 (along the diagonal of the silica pillars) (section II.2.2, Figure II.2-3).

Figure III.5-4 shows the dynamic contact angle of liquid lead on {20; 20} and {500; 500} samples in both directions d1 and d2. These two textures are such that the spreading diameter is respectively greater and smaller than the critical diameter. In both case, the dynamic contact angle evolves in the same way in any direction but with some differences. Most of the time, the dynamic contact angle obtained is greater in direction d1 than in direction d2.

Table III.5-2 shows the main contact angles as a function of the spreading direction (with the same notation as in Table III.3-1) for the different substrates. The difference between the angles measured in both directions (d1-d2) is given in the lines with a yellow background. The

measured initial contact angle θ_i and the advancing contact angle θ_a are in most cases (6 out of 9 patterned surfaces or 67%) higher in the direction d1 than in the direction d2. However the differences in the receding contact angles are less important and do not highlight the evidence of the influence of the measurement direction.



Figure III.5-4: Influence of spreading direction on dynamic contact angle of lead drop on a) {20; 20} substrates and b) {500; 500} substrates.

Table III.5-2: Contact angle of lead drop on patterned surfaces depending on spreading direction.

V ₀	d1·d2	$ heta_i$	θ_{dr}	θ_{da}	$ heta_f$	$ heta_r$	θ_a			
(m/s)	u1, u2	(°)	(°)	(°)	(°)	(°)	(°)			
	$\{5; 20\}, (f_{SiO_2} = 4\%)$									
0.81	d1	71±3	38±4	63±6	56±1	39	70			
0.91	d2	30±3	22±2	-	48±1	21	50			
	d1-d2	41±4	16±3	-	8±1	18	20			
		{	20; 100}	, $(f_{SiO_2} =$: 3%)					
0.78	d1	73±8	44±2	-	63±1	47	72			
0.83	d2	60±2	42±2	60±3	58±1	48	63			
	d1-d2	13±4	~0	-	5±1	-1	9			
		{	100; 500]	}, (f _{si02} =	= 3%)					
0.70	1-d1	42±5	26±4	59±4	59±2	39	63			
0.48	d2	65±6	50±4	89±5	69±1	61	101			
0.70	2-d1	53±5	40±6	51±3	56±1	48	57			
	2-d1-d2	-12±8	-10±7	-38±6	-13±1	-13	-44			
			<u>{5; 5}</u> , (j	$f_{SiO_2} = 2$	5%)					
0.69	d1	53±5	36±6	76±4	61±2	56	73			
		<u>{</u>	20; 20},	$(f_{SiO_2} =$	25%)					
0.90	d1	61±8	37±5	50±5	55±1	27	70			
0.71	d2	59±3	37±4	-	55±1	30	57			
	d1-d2	~0	~0	-	~0	-3	13			
		<u>{1</u>	00; 100}	$,(f_{SiO_{2}}=$: 25%)					
0.75	d1	66±6	47±5	88±6	69±3	56	97			
0.32	d2	39±2	31±6	58±3	55±1	35	61			
	d1-d2	27±4	16±8	30±7	14±3	21	36			
		<u>{5</u>	00; 500}	$, (f_{SiO_2} =$: 25%)					
0.54	d1	65±3	35±4	84±6	67±1	53	86			

0.59	d2	54±11	36±5	64±5	70±5	49	68				
	d1-d2	11±11	~0	20±8	~0	4	18				
$\underline{\{20;5\}}, (f_{SiO_2} = 64\%)$											
0.72	d1	83±5	66±5	105±5	99±1	80	109				
0.70	d2	74±6	61±5	114±4	99±2	89	114				
	d1-d2	9±8	~0	-9±6	~0	-9	-5				
$\{100; 20\}, (f_{SiO_2} = 69\%)$											
0.76	d1	76±6	54±4	111±4	108±1	77	111				
0.79	d2	75±7	62±4	121±6	125±3	95	139				
	d1-d2	~0	-8±6	-10±7	-17±3	-18	-28				
		<u>{5</u>	00; 100}	$,(f_{SiO_{2}}=$: 69%)						
0.66	d1	98±4	59±4	112±4	104±2	70	118				
0.39	d2	88±10	62±4	106±6	91±2	73	111				
	d1-d2	10±11	~0	6±7	13±3	-3	7				

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III.5.2.2. Solidified drops

At high temperatures, the final contact angle can only be observed in one direction for each experiment, due to the limitations of our experimental set-up. On the contrary, on the solidified drop, the influence of the spreading direction can be observed over the entire contour of the drop.

For this reason, the influence of the measurement direction on the spreading diameter and contact angle of the drop was studied on the solidified drop. The spreading diameters and contact angles were measured in forty directions around the drop in lateral view (section II.4.1).

Figure III.5-5 shows the influence of the measurement direction on the spreading diameter and contact angle of the drop on the $\{20; 20\}$ sample (25% of silica area fraction) and on the $\{20; 5\}$ sample (64% of silica area fraction) compared to pure substrates. The tests where the triple line was pinned during spreading are marked with the letter *p*.

Table III.5-3 summarizes the maximum, minimum and average values of the spreading diameter and contact angle of all undivided lead drops on patterned surfaces. In addition, the table shows (on a yellow background) the maximum spreading diameter of the drops in the

directions d1 (angle of view $\alpha_v = 0^\circ$, 90°, 180°, 270°) and d2 (angle of view $\alpha_v = 45^\circ$, 135°, 225°, 315°) in the lateral view.

As explained in section III.4, the effect of the stick-slip motion of the triple line during spreading leads to the elongated shape of the solidified drop on {20; 20} sample as on pure iron with $V_0 = 0.73 m/s$. On the other hand, the solidified drop on the {20; 5} sample is less deformed. The contact surface of the drop on the substrates almost circular. The same result is obtained for all surfaces with a high silica area fraction (64 to 69%). This is even the case for the {500,100} sample which could be subjected to deformation (section III.5.1).

The maximum spreading diameters are in most cases larger in the d1 direction than d2, especially when the triple line is pinned during receding at high temperature. The deformation of the triple line and therefore its pinning during receding seems to depend on the direction of the triple line in relation to the patterns. However, the differences are small and not far from the experimental error (± 0.04). These deformations could also depend on the fall of the lead drop (which is not perfectly identical for each test)

In Figure III.5-5 and Table III.5-3, the differences in the contact angle around the drop are less important compared to the measurement uncertainty and contact angle hysteresis. In fact, the differences in contact angle around the drop are related to the contact angle hysteresis.



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Figure III.5-5: Lateral view of solidified lead drop shape on patterned surfaces compared to the case of pure substrates. (a) Dimensionless drop diameter, (b) drop Contact angle depending on the angle of view α_{ν} .

Table III.5-3: Main parameters of the solidified lead drop shape from a lateral view on patterned surfaces.

V ₀ (m/s)	$\frac{D_{max}^l}{D_0}$	$\frac{D_{max}^{l}}{D_{0}}$ (d1)	$\frac{D_{max}^{l}}{D_{0}}$ (d2)	$\frac{D_{min}^l}{D_0}$	$\frac{D_m^l}{D_0}$	$\frac{D_f}{D_0}$	$ heta_{max}^l$ (°)	$ heta_{min}^l$ (°)	$ heta_m^l$ (°)	<i>θ</i> _f (°)
$\{5; 20\}, (f_{SiO_2} = 4\%)$										
0.81	1.70	1.65	1.67	1.39	1.57	1.67	65	46	55±4	56±1
				{100; 50	$00\}, (f_{sio_2} =$	3%)			•	
0.7	1.81	1.81	1.61	1.42	1.58±0.11	1.47	66	47	56±5	59±2
0.48	1.49	1.44	1.43	1.32	1.38±0.04	1.47	76	61	69±4	69±1
				{5;5},	$(f_{SiO_2} = 25)$	%)				
0.69	1.65	1.62	1.64	1.56	1.61±0.03	1.56	62	49	54±2	61±2
	$\{20; 20\}, (f_{SiO_2} = 25\%)$									
0.90	1.69	1.66	1.61	1.30	1.53±0.12	1.59	71	52	57±4	55±1
0.71	1.74	1.74	1.60	1.29	1.49±0.13	1.29	75	54	61±5	55±1
				{100; 10	$\{0\}, (f_{SiO_2} = 2)$	25%)	•		•	
0.75	1.42	1.42	1.37	1.24	1.35±0.05	1.47	78	65	73±3	69±3
0.32	1.70	1.70	1.60	1.52	1.60±0.05	1.71	59	45	51±3	55±1
				{500; 50	$\{0\}, (f_{SiO_2} = 2)$	25%)				
0.54	1.42	1.39	1.39	1.27	1.34±0.04	1.48	70	62	67±2	67±1
0.59	1.52	1.45	1.47	1.32	1.42±0.06	1.47	71	53	62±5	70±5
				{20; 5}	$,(f_{SiO_2}=64)$	-%)				
0.72	1.12	1.11	1.11	1.00	1.08±0.03	1.01	112	99	102±3	99±1
0.71	1.17	1.14	1.12	0.94	1.08±0.06	1.09	113	94	105±4	99±2
				{100; 20	$\{0\}, (f_{SiO_2} = 6)$	9 %)				

 $108\pm$ 0.76 109±5 1.11 1.08 1.10 0.98 1.05 ± 0.03 1.12 124 101 1 $125\pm$ 0.79 0.86 0.81 0.87 0.72 0.79 ± 0.04 0.79 135 121 128±3 3 $\{500;\,100\},\,(\pmb{f_{SiO_2}}=\pmb{69\%})$ 0.39 1.01 1.18 1.09 1.16 1.10 ± 0.04 1.22 107 100±6 91±2 86

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III.5.3 <u>Recapitulation</u>

It is well known that the wetting of a heterogeneous surface can vary according to the size of the drop in relation to the size of the defects. We estimated the surface area fraction covered by silica under the drop and the linear fraction of silica at the triple line for a circular contact surface of diameter D and patterned surfaces {d; s}. This theoretical calculation makes it possible to represent the ideal spreading of the drop, with the strong assumption that the drop is in thermodynamic equilibrium at all times. This calculation shows that the drop contact diameter must be at least five times larger than the size of the patterns (d+s) for the wetting to be independent of the position of the drop on the surface and of the spreading direction.

During the drop spreading, the advancing contact angles are more often larger in the spreading direction d1 than in the spreading direction d2. This result is surprising. Indeed, Naidich et al [84] also studied the influence of the spreading direction on the advancing and receding contact angles. If on the receding contact angles, the influence of the spreading direction is negligible in accordance with our result, they obtained larger advancing contact angles in the direction d2 than in the direction d1 (Figure I.4-4). The difference may be related to the difference in the method of measuring the advancing contact angles. In the work of Naidich et al, they were measured by heating up to the prescribed temperature the metal placed on the target surface.

On the solidified drop, deformations related to stick-slip motion phenomena were also found through a reconstruction of the drop in lateral view. When the drops are less circular, they are more elongated in the direction d1 than in the direction d2. This result is consistent with those obtained by Naidich et al.

Since the influence of the spreading direction is small and of the order of magnitude of the uncertainty of our measurements (due to different initial kinetic energies for example), we will only use an average of the data obtained on each texture in section III.6.

III.6 Influence of pattern size {d; s} at fixed silica area fraction

It is well-known that the area fraction of defects influence wetting of non-ideal surfaces (section I.1.6). However, the influence on the wetting of the defect size is not well-known. The surfaces studied in this work are made of silica of different sizes between 5 and 500 μ m. This gives the ability to study the influence of the size of the defects at high temperature.

Figure III.6-1 shows the dynamic contact angles of each patterned surface (3-4%, 25%, 64-70%) as a function of spreading time in relation to pure substrates (pure iron and pure silica). It should be noted that the results presented in this figure are average dynamic contact angles obtained from the two tests performed on each patterned surface (for more details see section III.3.2). For reasons of clarity, the errors are not shown.





Figure III.6-1: Influence of pattern size at fixed silica area fraction on dynamic contact angle: a) samples with low silica area fraction (3-4%), b) samples with moderate silica area fraction (25%) and c) samples with high silica area fraction.

From the images in Figure III.6-1, two main conclusions can be deduced.

First, at given silica area fraction, the dynamic contact angle is very close for all the patterned surfaces regardless of the size of the patterns (d) and their spacing (s). This shows that these two dimensional parameters of the patterned surfaces (d and s) have negligible effect on the wetting by liquid lead.

Then, we notice an influence of the silica area fraction. The dynamic contact angle on patterned samples with high silica area fraction is higher and closer to that of silica.

III.7 Influence of silica surface coverage

It has been demonstrated in the literature that the defects on the surface influence wetting (section I.1.6). In this section, the influence of the defect (silica) area fraction is studied on the final contact angles and on the contact angle hysteresis.

III.7.1 Final contact angle

In Figure III.7-1, the final contact angles obtained in our experiments are compared with the Cassie contact angle (Eq. (I.3.4)) as a function of the silica area fraction.

For surfaces with high silica area fraction (64 - 70%), the contact angle is close to the equilibrium contact angle predicted by Cassie's relationship: the drop is therefore close to its thermodynamic equilibrium state. For samples with a silica area fraction of 3% and 25%, the final contact angle is less than that predicted by the Cassie equation. On these samples, the drop appears to be retained in the contact angle hysteresis. The energy of the drop is not high enough to overcome the obstacles represented by silica pillars.



Figure III.7-1 Comparison between the Cassie contact angle (blue line) and the final contact of the tests presented in this work as a function of the surface fraction covered by silica. The textured iron / silica surfaces are represented by red squares, pure iron by a purple square and silica by a blue square.

III.7.2 Contact angle hysteresis on silica patterned surfaces

The contact angle hysteresis on patterned surfaces was measured using two methods (section II.3.6). In the first method, contact angle hysteresis were measured from the minimum contact angle (θ_{dr}) reached during the first receding of the liquid lead drop and the maximum contact angle (θ_{da}) when it advances again. In the second method, contact angle hysteresis (θ_r and θ_a) were measured at zero spreading velocity, taking into account all experimental points (e.g., Figure III.3-2b). The contact angle hysteresis obtained by both methods is given in Table III.3-1 for each sample and for each test.

In Figure III.7-2, these four contact angles measured on the patterned surfaces are compared to Cassie's contact angle and the advancing and receding contact angles predicted by Raj et al. [65] (section I.2.3). In the patterned surfaces {d; s} of this work, the most wetting defect (pure

iron) is interconnected. Therefore, according to Raj *et al.* $\lambda_{1max} = 1$ for undistorted triple contact line and $\lambda_{2max} = \frac{d}{d+s}$. With Eqs. (I.2.20) and (I.2.21), this leads to:

$$\cos\theta_r = \cos\theta_{Fe} \tag{III.7.1}$$

$$\cos \theta_a = \frac{d}{d+s} \cos \theta_{SiO_{2_a}} + \left(1 - \frac{d}{d+s}\right) \cos \theta_{Fe_a}$$
(III.7.2)

 θ_{Fe_r} and θ_{Fe_a} are the receding and advancing contact angles on pure iron and θ_{SiO_2a} is the advancing contact angle on pure silica.

The receding contact angles are almost constant for the low (3%) and moderate (25%) silica surface fractions. The dynamic receding contact angles θ_{dr} with high silica area fraction (~ 70%) remains of the same order of magnitude as that measured on pure iron. The same observation has been demonstrated by several authors in the literature (section I.4.2 [15], [65], [84]).

On patterned surfaces, one of the parameters that governs the contact angle hysteresis is the wetting of the solid, which is continuous. If the interconnected solid is the wettest one, the receding contact angle is constant up to a high area fraction occupied by the less wetted solid [23]. In our study, metallic iron is the interconnected solid, it is well wetted by liquid lead, which explains why the receding contact angle is of the same order of magnitude as the receding contact angle measured on pure iron. Indeed, when the liquid lead drop recedes on these samples, it remains pinned to the metallic iron parts as shown by the observations of the drop triple contact line (section III.4.2).

The receding contact angles measured at the end of the first receding step of the drop are in very good agreement with the model of Raj et al. [23]. It should be noted that the receding contact angles measured by the two methods are slightly different. This may be related to the dispersion of the contact angle and the difficulty to accurately measure the contact angle hysteresis.

The advancing contact angles are closer to the equilibrium contact angle predicted by Cassie's model and therefore slightly overestimated by Raj et al.



Figure III.7-2: Contact angle hysteresis of liquid lead on silica-patterned iron surface relative to the Cassie contact angle (blue line) and the prediction of Raj et al. [65], as a function of silica surface fraction. The receding contact angles are found in empty squares and the advancing contact angles in solid black squares.

III.8 Conclusion

Using the dispensed drop technique, wetting experiments by liquid lead on heterogeneous surfaces were performed at 450°C. The heterogeneous surfaces were silica-patterned surfaces composed of regular silica-patterned high-purity iron with different pillar sizes (from 5 to 500 μ m) and spacing (from 5 to 500 μ m). In this solid/iron system, iron is wetted by liquid lead (equilibrium contact angle of 55°) whereas silica is not (equilibrium contact angle of 135°).

First, for all samples, the drop spreads and a maximum spreading diameter is reached. The lead drop then recedes and different wetting types have been observed. In some cases, the drop advances again before oscillating and stabilizing to its final state. In other cases, the drop is pinned during its receding and the triple line spreads by stick-slip motion on the sample.

Only the first case was observed on surfaces with high silica surface coverage. The lead drop was close to the most stable contact angle or equilibrium contact angle.

On surfaces with moderate silica area fraction, both cases of wetting (stick-slip motion or not) were observed. Stick-slip motion was commonly observed on samples with low silica surface coverage. In this case, the triple line can be strongly deformed during its receding, which can lead to its division into several droplets. Image processing and scanning electron microscopy showed that the triple contact line was mainly on pure iron, avoiding silica pillars.

When the drop is strongly deformed, it is more elongated in the direction d1 than in the direction d2. But the influence of the spreading direction of the triple contact line relative to the patterns on the wetting was found to be small. The spreading diameter and contact angle measured at low and high temperatures were in good agreement, which led us to conclude that the drop remains representative of the high temperature wetting parameters after solidification.

With respect to the effect of oxide size and their distribution, the same spreading dynamics was observed on the different patterned surfaces for a given oxide area fraction. In addition, the same results were observed on the solidified drop. These results confirm that the defect area fraction plays a key role in wetting but not the size or distribution of defects.

Finally, we analysed the influence of the surface area fraction covered by silica on the final contact angle and on the contact angle hysteresis. The final contact angle, especially for samples with a moderate silica surface fraction is close to a receding contact angle due to the pinning effect. The receding contact angles were almost constant, in agreement with literature results. Indeed, it is generally admitted that the receding contact angle is constant on the patterned sample where the more wetting solid is interconnected [14], [15], [65], [84] due to the pinning effect on the most wetting defect during the receding phase.

Chapter III: Wetting of liquid lead on patterned surfaces

Chapter IV: Wetting dynamics and discussions

IV Wetting dynamics and discussions

IV.1 Introduction

As explained in Chapter 3, the wetting dynamics of liquid lead on silica patterned iron surfaces can be divided into four different phases (Figure IV.1-1). First, the drop spreads upon impact until it reaches its maximum spreading diameter (1). Then, the drop recedes (2). Last, it undergoes some oscillations of lower amplitude until rest. At the beginning of this relaxation, the contact line moves as the drop oscillates (3). This motion is affected by pinning and depinning events: a stick-slip motion is observed. Finally, the contact line stops permanently and the drop oscillates with fixed contact line (4) until resting state.



(a) Pure iron,
$$V_0 = 0.75 \text{ m/s}$$



Figure IV.1-1: Spreading contact diameter of lead droplets normalized by that of the spherical droplets before impact. The inserted pictures show the shape of the droplets at the different stages of spreading: (a) pure iron, (b) patterned surface {500; 100}. In (a) the different phases of the spreading dynamics are delimited: (1) Spreading phase, (2) first receding, (3) oscillations with moving contact line, (4) oscillations with fixed contact line

Figure IV.1-2 shows that the receding and the relaxation of the drop depend on the surface wettability. We may distinguish two cases:

- Relaxation with moderate damping. This case is often observed on patterned surfaces with high silica area fraction, characterized by a high contact angle (low wettability, {500; 100} in Figure IV.1-2).
- Relaxation with high damping. This case was observed on samples with low and moderate silica area fractions: wetting of {20; 20} and {100; 500} samples in Figure IV.1-2. This high damping is due to strong pinning effects. Because of the pinning events, the drop can split into two or more droplets ({100; 500}).

Chapter IV: Wetting dynamics and discussions



Figure IV.1-2: Different relaxation cases observed on patterned surfaces.

In this chapter, we aim to model the different phases of the drop dynamics. We are looking for simple analytical models. Our approach is based on simplified mass and energy balances. This requires some simplifying assumptions:

- (i) The wetting phenomena associated with the spreading/retraction of the drop on the patterned surfaces are described from a macroscopic point of view.
- (ii) We neglect the distortions of the contact line and assume that the line is axisymmetric and solely characterized by its radius.
- (iii) The drop takes simple axisymmetric shapes such as pancake or spherical cap shape.

We emphasize that the details of the silica patterns are missed in the present approach. The wetting is solely described by three angles: the equilibrium contact angle θ_E , the advancing contact angle θ_a and the receding contact angle θ_r .

The theoretical equilibrium contact angle satisfies Cassie's law:

$$\cos \theta_E = f_s \cos \theta_{SiO2} + (1 - f_s) \cos \theta_{Fe} \tag{IV.1.1}$$

where the silica area fraction on {d; s} patterned surfaces reads:

$$f_s = \left(\frac{d}{d+s}\right)^2 \tag{IV.1.2}$$

The advancing and receding contact angles are either measured or estimated from Raj et al. model [65]. Since Raj et al. consider heterogeneous surfaces patterned with discs, we may approximate the squares of the silica patterned iron surfaces either with the circle inscribed in the square or with the circumscribed circle. In the former case, the silica linear fraction is given by:

$$\lambda_s = \frac{d}{d+s} \tag{IV.1.3}$$

In the latter case, the silica linear fraction is given by:

$$\lambda_s = \frac{\sqrt{2}d}{\sqrt{2}d + s} \tag{IV.1.4}$$

According to Raj et al. model, the advancing contact angle reads, in the case of non-wetting defects:

$$\cos \theta_a = \lambda_s \cos \theta_{SiO2} + (1 - \lambda_s) \cos \theta_{Fe} \tag{IV.1.5}$$

The receding contact angle is given by:

$$\cos\theta_r = \cos\theta_{Fe} \tag{IV.1.6}$$

We note that this expression is no more valid when the silica surface fraction tends to 1.

IV.2 Spreading phase

In this section, we first identify the regime and the characteristic time scale of the spreading phase. Then, we determine the scaling law verified by the maximum spreading diameter. Finally, these results are aggregated to describe the evolution of the spreading diameter over time.

IV.2.1 <u>Characteristic time scale [1]</u>

In the wetting device used here, the liquid metal drop is dispensed on the solid substrate at an impact velocity V_0 of about 0.7 *m.s*⁻¹. Based on the forces that promote and oppose drop
spreading during the first spreading phase, Schiaffino and Sonin [101] proposed a classification of the different types of liquid drop impact according to two dimensionless numbers: the Ohnesorge number (Oh) and the Weber number (We):

$$Oh = \frac{\mu}{\sqrt{\rho D_0 \gamma}} = \frac{\sqrt{We}}{Re}$$
(IV.2.1)

$$We = \frac{\rho D_0 V_0^2}{\gamma} \tag{IV.2.2}$$

The Weber number *We* compares inertial and capillary forces and scales the driving force for the droplet's spreading. The Ohnesorge number *Oh* is the ratio of the viscous force to the inertia and surface forces and scales the force that resists the spreading.

It should be noted Vadillo [91] and Laan et al. [102] use the drop initial diameter D_0 whereas Bartolo et al. and Schiaffino and Sonin use the drop initial radius.

When the liquid spreads with a moderate contact angle, i.e., angles that are not too close to 0 or π , the plane (*We*, *Oh*) can be divided into four asymptotic regions (Figure IV.2-1). In the case of a high *We*, the liquid drop is driven radially outward by the dynamic pressure gradient induced by the impact; in the case of a low *We*, it is pulled out by the capillary force at the contact line. At high *Oh*, the resistance is caused by viscous friction and at low *Oh*, the resistance is due to the inertia.

Our experimental data ($Oh = 5.8 \times 10^{-4}$, We = 6 - 49) are in region I of the plane (Oh, We). In this region, the droplet spreading upon impact (phase 1) is mainly driven by the impact velocity and the spreading resistance is due to inertia. Thus, the characteristic time scale for spreading is the inertial time t_i :

$$t_i = \frac{D_0}{V_0} \tag{IV.2.3}$$



Figure IV.2-1: Our experimental data in the classification of drop impact proposed by [101]

IV.2.2 Maximum spreading diameter

At the end of the spreading phase, the drop reaches its maximal diameter. The maximum spreading diameter depends on the impact velocity. When a droplet is put in contact with a solid, its initial kinetic energy can be dissipated by viscosity or stored in deformation during the impact. The spreading diameter can be calculated by writing the energy conservation from the time of impact to the time the drop reaches its maximum spreading diameter. The maximum spreading diameter is found to be a function of two dimensionless numbers: the Weber number (*We*) which is the ratio between the inertial and the capillary force and the Reynold number (*Re*) which is the ratio between the inertial and the viscous force.

$$\frac{D_{max}}{D_0} = f\left(We = \frac{\rho D_0 {V_0}^2}{\gamma}, Re = \frac{\rho D_0 V_0}{\mu}\right)$$
(IV.2.4)

Depending on the value of these dimensionless numbers, two asymptotic regimes can be distinguished:

- the viscous regime when $We \gg \sqrt{Re}$
- the capillary regime when $We \ll \sqrt{Re}$

In the viscous regime, the initial kinetic energy of the drop is mainly dissipated by viscosity. The maximal spreading diameter scales as $D_0 \operatorname{Re}^{1/4}$ or $D_0 \operatorname{Re}^{1/5}$ as often proposed in the literature [103]–[105]. In the capillary regime, i.e. when the initial kinetic energy of the drop is completely converted into surface energy, the maximal spreading diameter scales as $D_0 We^{1/2}$.

Figure IV.2-2 shows the maximum spreading diameter as a function of (a) Reynolds number (*Re*) and (b) Weber number (*We*) in comparison with the scaling laws. The figure also shows earlier data from Laan et al [102] and Clanet et al [105]. In the work of Laan et al the solid surfaces were partially wettable: rolled stainless-steel surfaces with a contact angle θ between 80° and 90°. The liquid drops were either viscous (water-glycerol 51 mPas) or inviscid (water). Clanet et al studied inviscid drop (water or mercury) on super-hydrophobic surfaces (θ ~160°) and partially wettable surfaces (θ ~90°).

In Figure IV.2-2a, the data of the viscous drop of water-glycerol 51 mPas (full red circles) fit quite well to the model. However, our experimental points ($\mu = 2$ mPas) in full purple circles as well as the data of inviscid drop [102] are not described by the two viscous scaling laws. This suggests that other forms of non-viscous dissipation occur during the spreading of inviscid drops.

In the capillary regime (Figure IV.2-2b), the classical scaling law in $D_0We^{1/2}$ also poorly predicts the data of inviscid drops. While, the scaling law in $D_0We^{1/4}$ proposed by Clanet et al [105] predicts quite well the experimental points of both our data and those of Clanet et al. Notwithstanding this result, we can observe a dispersion of the experimental points around the model.



(b)



Figure IV.2-2: Dimensionless maximum contact diameter as function of: (a) Reynold number in the viscous regime and (b) Weber number in the capillary regime. Our experimental data are shown together with the work of Laan et al [102] and Clanet et al [105].

This discrepancy could be explained by the fact that the model does not account for the wettability of the surfaces. In fact, it has been well demonstrated that the wettability of the surface influences the maximum spreading diameter [103], [104], [106]–[108].

Thus, we rewrote the model in capillary regime by considering the surface wettability. It led in a correction of the Weber number $We' = \frac{We}{(1-\cos\theta)}$, where θ is the equilibrium contact angle. The same correction was proposed by M. Zaidi [1] and J. Diawara [2] in their thesis works (appendix D). In Figure IV.2-3, the revisited model with the final contact angle θ_f correctly describes the maximum spreading diameter of inviscid drops.



Figure IV.2-3: Maximum spreading diameter as a function of the Weber number modified to consider the contact angle of the drop on the substrate.

In this case, the maximum spreading diameter writes:

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$$\frac{D_{max}}{D_0} = c_{dm} \left(\frac{We}{1 - \cos\theta}\right)^{1/4} \tag{IV.2.5}$$

Where c_{dm} is a fitting constant obtained by means of a least-squares fit. It is equal to $c_{dm} = 1.07$ with the coefficient of determination $R^2 = 0.75$ for our experimental points and $c_{dm} = 1.01$ with the coefficient of determination $R^2 = 0.93$ for the data of Clanet et al [105].

If the maximum dimensionless spreading diameter scales as $We^{1/4}$, it means that all three forces (inertial, viscous and capillary) are important. For this reason, neither a simple viscous nor a capillary scaling is observed. Laan et al [102] developed a crossover model between the two regimes. In their model, the maximum spreading diameter is written according to a single dimensionless number called the impact number, P_I :

$$P_I = \frac{We}{Re^{\frac{2}{5}}}$$
(IV.2.6)

which scales the Weber number and Reynolds number.

By using an interpolation between the $We^{\frac{1}{2}}$ and $Re^{\frac{1}{5}}$ classical laws, we can write:

$$\frac{D_{max}}{D_0} \propto Re^{\frac{1}{5}} \mathcal{F}\left(WeRe^{-\frac{2}{5}}\right) = Re^{\frac{1}{5}} \mathcal{F}(P_I)$$
(IV.2.7)

where \mathcal{F} is a function of the parameter $WeRe^{-\frac{2}{5}}$. Within the high-viscosity limit $(P_I \gg 1)$, $\mathcal{F}(P) \sim 1$ should be found to satisfy the relationship $D_{max}/D_0 \propto Re^{1/5}$. Whereas, in the capillary regime $(P_I \ll 1)$, $\mathcal{F}(P)$ must scale as $\mathcal{F}(P) \propto P_I^{1/2}$ to recover the law $D_{max}/D_0 \propto We^{1/2}$.

In the intermediate regime (impact number around unit), Laan et al [102] calculated the crossover model between the two asymptotic regimes using a Padé approximant.

$$\mathcal{F}(P) = \frac{P_I^{1/2}}{P_I^{1/2} + c_{mp}}$$
(IV.2.8)

where c_{mp} is a fitting constant obtained by means of a least-squares fit.

Then, the model reads as follows:

$$\frac{D_{max}}{D_0} R e^{-\frac{1}{5}} = \frac{P_I^{1/2}}{P_I^{1/2} + c_{mp}} \quad c_{mp} \approx 1$$
(IV.2.9)

However, this model originally developed for partially wetting surfaces is not suitable for drops that wet substrates with a low contact angle. Then, to take into account for surface wettability, Eq.(IV.2.9) can be modified by analogy with the energy model (Figure 2.4):

$$\frac{D_{max}}{D_0} R e^{-\frac{1}{5}} = \frac{{P_I}'^{1/2}}{{P_I}'^{1/2} + c_{mp}}; \quad P_I' = \frac{P_I}{1 - \cos\theta}, \qquad c_{mp} \approx 1$$
(IV.2.10)

The fit of Eq. (IV.2.10) is consistent with our data but also with those of Bartolo et al [109] of water glycerol mixtures on non-wetting surfaces and Laan et al [102] of water droplets deposited on partially non-wetting surfaces, in Figure IV.2-4. Originally the contact angle in the model is the equilibrium contact angle (given by the classical law of Cassie), however for our data the best fitting was obtained with the final contact angle.

These analyses show that the initial spreading of the liquid lead drop is neither in the viscous nor in the capillary regime. The droplet spreading on impact is dominated by the three forces of inertia, viscosity and capillarity [102], [105].



Figure IV.2-4: Rescaled maximum spreading ratio as function of impact number for our data and those of Bartolo et al [109] (water glycerol mixtures on nonwetting surfaces) and Laan et al [102] (water droplets deposited on rolled stainless-steel surfaces with a contact angle between 80° and 90°). The solid line shows the Padé approximant function Eq. (IV.2.10) fitted to the experimental data with $c_{mp} = 1.05$.

IV.2.3 Model of spreading diameter

During the spreading phase for which $t < t_i$, several authors have reported that the transient spreading diameter evolves roughly as the square root of time [106], [110]–[112].

In fact, in this phase, the drop could be considered as a spherical cap of liquid spreading into a cylindrical disk of diameter D and thickness h_d .

The Liquid flows from the drop, shaped like a truncated sphere, into the film through an area of diameter d_s with velocity V_0 .



Figure IV.2-5: A model of a drop spreading. Inspired from [103].

Using mass conservation, the velocity at the edge of the cylindrical disk is given by the relation:

$$V_0 d_s^2 = 4Dh_d U \tag{IV.2.11}$$

Assuming the thickness h_d of the cylindrical disk constant during the spreading (in the case of very small contact angle), at the maximum spreading diameter, we can write:

$$h_d = \frac{2D_0^3}{3D_{max}^2}$$
(IV.2.12)

Moreover, the diameter d_s of the spherical part of the drop varies from 0 to D_0 during the spreading with a mean value of $D_0/2$.

Then, setting $U = \frac{dD}{2dt}$ and combining Eq.(IV.2.11) and Eq.(IV.2.12), we obtain a scaling power law as:

$$\frac{D}{D_{max}} = \sqrt{\frac{3}{8} \frac{t}{t_i}} = \sqrt{\frac{t}{t_i'}} \qquad t_i' = \frac{8}{3} t_i$$
(IV.2.13)

The maximum spreading diameter is given by Eq.(IV.2.5), then the last equation becomes

$$\frac{D}{D_0} \approx c_{mp} \left(\frac{We}{1 - \cos\theta}\right)^{1/4} \sqrt{\frac{t}{t_i'}} = \alpha_{mp} \left(\frac{t}{t_i'}\right)^{a_s}, a_s = 1/2$$
(IV.2.14)

where

$$\alpha_{mp} = c_{mp} \left(\frac{We}{1 - \cos\theta}\right)^{1/4} \tag{IV.2.15}$$

This time evolution in square root of the drop contact diameter during the first spreading phase has been widely validated [104], [107], [108], [110], [91], [145].

If the effect of surface wettability is negligible on the spreading which is mainly driven by the impact pressure, the drop is slowed at the end of the spreading by viscous and capillarity effects until the maximum spreading diameter is reached.



Figure IV.2-6. A drop spreading on solid surface a) just after the impact, b) at maximum spreading diameter.

To analyse the applicability of this model in power ½ to our experimental data, we plotted the dimensionless spreading diameter of the drop as a function of the dimensionless time $\frac{t}{t_i}$ for each set of our study, in Figure IV.2-7. On the same figure, we also reported data from Vadillo et al [106] and Rioboo et al [112]. Both studied the wetting of water on the glass at velocity impact close to ours. For each set of data in the Figure IV.2-7, the obtained fitting parameters (α, a_s) of Eq. (IV.2.14) and the corresponding standard deviation are shown in Table IV.2-1. The fitting is significantly good (coefficient of correlation R² > 0.97, in most of cases). In all cases, a_s was found to be of the order of magnitude of ½. These results confirm that, in the first spreading phase, the power law $t^{1/2}$ correctly describes the drop spreading diameter.

Sample	V ₀ (m/s)	θ(°)	a _s	Standard deviation of <i>a_s</i>	$lpha_{mp}$	Standard deviation of α_{mp}	R ²
Fe	0.75	52	0.55	0.02	3.78	1.02	0.99
Fe	0.73	55	0.49	0.03	3.56	1.02	0.97
Fe	0.60	55	0.68	0.02	3.78	1.02	0.99
{5; 20}	0.81	56	0.60	0.05	3.71	1.03	0.95
{5; 20}	0.91	48	0.55	0.04	4.22	1.03	0.97
{20; 100}	0.78	63	0.49	0.04	3.71	1.03	0.97
{20; 100}	0.83	58	0.45	0.03	3.97	1.02	0.98
{100; 500}	0.70	59	0.52	0.03	3.78	1.02	0.98
{100; 500}	0.48	69	0.69	0.08	3.53	1.08	0.95
{100; 500}	0.70	56	0.45	0.02	3.78	1.02	0.98
{5;5}	0.69	61	0.64	0.06	3.25	1.04	0.96
{20; 20}	0.90	55	0.47	0.03	3.35	1.03	0.98
{20; 20}	0.71	55	0.36	0.01	2.66	1.01	0.99
{100; 100}	0.75	69	0.59	0.06	3.63	1.05	0.95
{100; 100}	0.32	55	0.52	0.08	3.03	1.06	0.92
{500; 500}	0.54	67	0.57	0.05	3.74	1.06	0.96
{500; 500}	0.59	70	0.62	0.04	3.67	1.04	0.97

Table IV.2-1: Fitting parameters of the power law model Eq. (IV.2.14). Comparison between our data and the low temperature data from Vadillo et al [91][106] *and Rioboo et al* [112].

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{20; 5}	0.72	99	0.42	0.03	2.66	1.02	0.98
{20; 5}	0.70	99	0.51	0.03	3.22	1.03	0.98
{100; 20}	0.76	108	0.64	0.03	2.80	1.03	0.99
{100; 20}	0.79	125	0.49	0.04	3.53	1.04	0.98
{500; 100}	0.66	104	0.61	0.13	3.82	1.02	0.85
{500; 100}	0.39	91	0.64	0.06	2.59	1.06	0.96
Silica	0.60	134	0.47	0.01	3.03	1.01	0.99
Silica	0.86	137	0.56	0.1	3.16	1.12	0.83
Water/glass [91][106]	1.00	50	0.48	0.01	4.10	1.02	0.98
Water/glass [112]	0.82	58	0.35	0.01	3.00	1.02	0.98

However, the coefficient α is not well determined as the corresponding standard deviation for each set of data is not negligible (Table IV.2-1). In addition, in Figure IV.2-7, on can observe the influence of the surface wettability. This influence could be modelled by Eq.(IV.2.15).

To study the relevance of this model, Figure IV.2-8 shows the dimensionless spreading diameter divided by the theoretical coefficient α_{mp} (given by Eq.(IV.2.15)): $\left(\frac{D}{D_0}\right)\frac{1}{\alpha_{mp}}$ as function of dimensionless time $\frac{t}{t_i'}$, in a logarithmic scale. In this figure, all the studied data collapse on the same line of slope 1.2.

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Figure IV.2-7: Spreading diameter as function of time in In-In scale.



Figure IV.2-8: Dimensionless spreading diameter divided by the theoretical coefficient α as function of dimensionless time, in logarithmic scale.

IV.3 First receding

At the onset of retraction, we observe that the drops are shaped like a pancake (see Figure IV.1-1). This shape differs from the one reported by Bartolo et al. [109] in region I of the (Oh, We)-plane. In the latter case, the drop consists of a thin liquid film surrounded by a donut-shaped rim which contains most of the liquid. This difference is attributed to stronger inertial effects in Bartolo et al. experiments. Indeed, Bartolo et al. experiments (for the part performed in region I) are characterized by higher values of the Weber number, *i.e.* from about 15 to about 320 whereas *We* ranges from 6 to 49 in the present experiments.

As a result, the Taylor-Culick approach used by Bartolo et al. to describe the drop retraction cannot be applied to our experiments.

Our goal is now to describe the receding of a pancake-shaped drop. The total energy of the drop is the sum of gravitational energy E_g , surface energy E_s and kinetic energy E_c . Dissipation results from viscous effect (E_v) and contact angle hysteresis (E_h).

Hence, the energy balance reads:

$$\frac{d}{dt}(E_s + E_g + E_c) = -\frac{d}{dt}(E_v + E_h)$$
(IV.3.1)

Gravitational effect can be reasonably neglected since the typical film thickness at the onset of retraction is about one order of magnitude lower than the critical thickness $\varepsilon_c = 2\kappa^{-1}\sin(\theta_E/2)$ where $\kappa^{-1} = \sqrt{\gamma/(\rho g)}$ is the capillary length. ε_c is the thickness of a liquid puddle flattened by gravity [4]. As an example, for a {5; 20} sample, the film thickness at the onset of retraction is equal to $H = 0.38 \ mm$ whereas the critical thickness is equal to $\varepsilon_c \approx 2 \ mm$. Viscous effects are negligible since (i) the Ohnesorge number is very low, *i.e.* $Oh = 5.8 \times 10^{-4}$, (ii) hysteresis dissipation dominates over viscous dissipation. These assumptions will be further checked in the section IV.4.

So the energy balance is written:

$$\frac{d}{dt}(E_s + E_c) = -\frac{d}{dt}(E_h) \tag{IV.3.2}$$

Surface energy Es

For a displacement dR of the drop contact line, the associated variation of the surface energy is given by:

$$dE_s \cong 2\pi R dR \gamma_{SL} + 2\pi R dR \gamma - 2\pi R dR \gamma_{SV}$$
(IV.3.3)

as long as the puddle thickness remains low compared to its diameter.

By introducing θ_E the equilibrium contact angle of the drop on the solid surface, Eq. (IV.3.3) reads:

$$dE_s \cong 2\pi R dR\gamma (1 - \cos \theta_E) \tag{IV.3.4}$$

<u>Kinetic energy E_c</u>

We express the kinetic energy in the limit of a puddle-shaped drop, *i.e.* $H \ll R$. We consider the same simple flow as Noblin *et al.* [115] did to study the oscillations of a puddle flattened by gravity. In the present case, the puddle is not flattened by gravity but by the impact of the

drop on the solid surface. The radial and vertical velocities of the liquid (of density ρ) expresses as follows:

$$v_r = \frac{r}{R} \frac{dR}{dt}, \quad v_z = -2\frac{z}{R} \frac{dR}{dt}$$
(IV.3.5)

where the velocity field satisfies the continuity equation and the no-slip condition at the solid/liquid interface. Then, the kinetic-energy density reads:

$$e_c = \frac{1}{2} \frac{\rho}{R^2} \left(\frac{dR}{dt}\right)^2 (r^2 + 4z^2)$$
(IV.3.6)

By integrating this equation over the entire volume of the drop, we obtain:

$$E_c = \frac{1}{4} \rho V_{drop} \left(\frac{dR}{dt}\right)^2 \left[1 + \frac{8}{3} \left(\frac{H}{R}\right)^2\right]$$
(IV.3.7)

In the puddle limit, i.e. $H(t) \gg R(t)$, the kinetic energy reduces to:

$$E_c \approx \frac{1}{4} \rho V_{drop} \left(\frac{dR}{dt}\right)^2 \tag{IV.3.8}$$

Hysteretic dissipation E_h

During receding, a part of the drop energy is lost due to the contact angle hysteresis:

$$dE_h = 2\pi R \, sg(dR) \, \gamma(\cos\theta_r - \cos\theta_E) = 2\pi R dR \gamma(\cos\theta_E - \cos\theta_r)$$
(IV.3.9)

where θ_r is the receding angle. θ_r is either measured or estimated using the Raj et al. model [65] (see chapter I, section 3.3).

Using Eqs. (IV.3.4), (IV.3.8) and (IV.3.9), the energy balance becomes:

$$\frac{1}{2}\rho V_{drop}\frac{d^2R}{dt^2} + 2\pi R\gamma (1 - \cos\theta_r) = 0$$
(IV.3.10)

The solution of this equation reads:

$$\frac{D}{D_{max}} = \frac{R}{R_{max}} = \cos\left(\sqrt{\frac{4\pi\gamma(1-\cos\theta_r)}{\rho V_{drop}}}t\right)$$
(IV.3.11)

where the origin of time coincides with the time when the spreading is maximal. We emphasize that expression of Eq.(IV.3.11) is valid as long as the thickness of the drop remains small in front of its diameter, *i.e.* at the beginning of the first receding.

We deduce the characteristic time τ_r of the first receding:

$$\tau_r = \sqrt{\frac{\pi \rho V_{drop}}{\gamma (1 - \cos \theta_r)}}$$
(IV.3.12)

This time corresponds to the inertial-capillary timescale of the drop in contact with the solid surface. It is identical to the characteristic time found by Bartolo et al. [109] using Taylor-Culick approach. τ_r ranges between 24 ms for lead drop receding on {20;5} silica-patterned iron surface up to 40 ms on pure iron surface.

Figure IV.3-1 shows the variations of the acosine of the dimensioless drop diameter $a\cos(D/D_{max})$ as a function of t/τ_r , i.e. the time made dimensioless by τ_r . These variations are reported for liquid lead drops spread upon impact on the different surfaces studied in this work: pure iron and silica and patterned surfaces iron-silica. The origin of time coincides systematically with the time when the spreading is maximal and τ_r is calculated according to Eq.(IV.3.12) with θ_r the receding angle measured in the experiments. First, it appears that all the data collapse onto the same curve from the onset of retraction up to $t \cong 0.1 \times \tau_r$. We conclude that τ_r (as given by Eq.(IV.3.12)) is the appropriate timescale at the beginning of the first receding. In the other hand, a single straight line obtained from the onset of retraction up to $t \cong 0.1 \times \tau_r$ confirm that Eq.(IV.3.11) correctly describes drop contact diameter in the first moments of the receding. After that, the puddle approximation used to estimate the variations

of the drop surface energy is no more valid (the shape of the drop is then closer to a spherical cap than to a puddle) and the model no longer correctly reproduces the behaviour of the drop.



Figure IV.3-1: Variations of $acos(D/D_{max})$ as a function of t/τ_r for liquid lead drops spread upon impact each patterned surface studied in this work: first moments of the receding.

IV.4 Drop oscillations with moving contact line

As a liquid drop relaxes toward equilibrium, it first undergoes oscillations with moving contact line (1st kind), followed by oscillations with fixed contact line (2nd kind) until rest. Figure IV.4-1 shows that the number of the oscillations of the 1st kind increases as the wettability of the solid surface decreases. Furthermore, these oscillations exhibit a stick-slip motion. This motion is clearly visible for the drops relaxing on silica-patterned iron surface. In this case, the stick events are due to the contact line anchorage on the pure iron strips.



Figure IV.4-1: Relaxation of liquid lead drops spread upon impact on pure substrates (iron and silica) and two patterned surfaces ({500; 500} and {20; 5}): oscillations with moving contact line (1st kind).

We would like to determine (i) the pulsation of the oscillations of the 1st kind and (ii) the transition criterion between the oscillations of 1st kind and the oscillations of 2nd kind. To our knowledge, this configuration has been studied very little, with the notable exception of the article by Noblin et al. [115]: they investigated the effects of vertical vibrations on non-wetting large water drops flattened by gravity and further examined the transition between pinned and mobile contact line oscillations.

We presently consider the simple case of a sessile drop in the shape of a spherical cap and focus on the first mode (n = 1) of these oscillations. We will see that the spherical cap assumption is valid for some motions of the drop if the drop is small enough (*i.e.* if the gravity effects are negligible in front of the capillary effects).

We remind that the drop energy balance reads

$$\frac{d}{dt}(E_s + E_g + E_c) = -\frac{d}{dt}(E_v + E_h)$$
(IV.4.1)

where the total energy of the drop is the sum of the surface energy E_s , the gravitational energy E_g and the kinetic energy E_c , and the energy losses result from viscous dissipation (E_v) within the liquid phase and contact angle hysteresis (E_h) .

In the following, we first report some useful mathematical relationships associated with the spherical cap geometry [116]. Then, we express each of the terms of Eq. (IV.4.1) and finally we derive the dynamic equation of the oscillating drop with mobile contact line.

IV.4.1 Spherical cap

Throughout its relaxation, the drop is approximated as a spherical cap with a varying radius and a constant volume V_{drop} (Figure IV.4-2). The spherical cap is characterized by its contact radius R = D/2, its height *H*, its geometric contact angle θ and its radius of curvature R_s .



Figure IV.4-2: Geometric parameters of a spherical cap.

These geometrical parameters are related through the following equations:

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$$\sin\theta = \frac{R}{R_s} \tag{IV.4.2}$$

$$\cos \theta = \frac{1 - (H^2/R^2)}{1 + (H^2/R^2)}$$
(IV.4.3)

$$H = R_s(1 - \cos\theta) \tag{IV.4.4}$$

$$V_{drop} = \frac{\pi}{6} H(3R^2 + H^2)$$
(IV.4.5)

Then, we may express the radius *R* of the spherical cap as a function of the geometric contact angle θ :

$$R = \left(\frac{3V_{drop}}{\pi}\right)^{1/3} \frac{(1+\cos\theta)^{1/2}}{(2+\cos\theta)^{1/3}(1-\cos\theta)^{1/6}}$$
(IV.4.6)

The position \bar{z} of the center of mass with respect to the center of the sphere (radius R_s) is given by:

$$\bar{z} = \frac{3}{4} \frac{(2R_s - H)^2}{3R_s - H}$$
(IV.4.7)

Thus, the altitude z_{CM} of the center of mass above the solid surface reads:

$$z_{CM} = \frac{3}{4} \frac{(2R_s - H)^2}{3R_s - H} + H - R_s$$
(IV.4.8)

IV.4.2 Energy contributions

Surface energy Es

For a displacement dR of the drop contact line, the associated variation of the surface energy reads:

$dE_s = 2\pi R dR\gamma_{SL} + 2\pi R dR\gamma \cos\theta - 2\pi R dR\gamma_{SV}$ (IV.4.9)

where the geometric contact angle of the spherical cap is the dynamic contact angle of the drop. It should be noted that the variation of the liquid/vapor interface area is exactly equal to $2\pi R dR\gamma \cos \theta$ for a spherical cap of constant volume [117].

We introduce the equilibrium contact angle θ_E of the system. θ_E is given by the Young-Dupré law for liquid lead on pure iron or pure silica surfaces, and by the Cassie law (see chapter 1, section 3.1) for liquid lead on silica-patterned iron surfaces. Then, Eq. (IV.4.9) becomes:

$$dE_s = 2\pi R dR\gamma(\cos\theta - \cos\theta_E) \tag{IV.4.10}$$

It should be noted that the spherical cap assumption is relevant as long as the drop recedes (resp. advances) with a contact radius greater (resp. lower) than the equilibrium contact radius R_E . The drop cannot strictly keep its spherical cap shape when it recedes (resp. advances) with a contact radius lower (resp. greater) than R_E . Indeed, the geometric contact angle of the cap is then greater (lower) than θ_E whereas the receding (advancing) dynamic contact angle has to be lower (greater) than θ_E .

Gravitational energy Eg

The gravitational energy rate is related to the drop center of mass motion and is given by:

$$\frac{dE_g}{dt} = \rho V_{drop} \frac{dz_{CM}}{dt} g \tag{IV.4.11}$$

Kinetic energy E_c

The kinetic energy of the drop is simply expressed in the limit of small contact angles. In that case, the contact radius of the drop is much greater than its height and we can reasonably use the puddle approximation set out in section IV.3:

$$E_c \cong \frac{1}{4} \rho V_{drop} \left(\frac{dR}{dt}\right)^2 \tag{IV.4.12}$$

The kinetic energy rate reads:

$$\frac{dE_c}{dt} \approx \frac{1}{2} \rho V_{drop} \frac{dR}{dt} \frac{d^2 R}{dt^2}$$
(IV.4.13)

Viscous dissipation E_p

According to [118], the viscous dissipation rate reads in cylindrical coordinates:

$$\Phi = \mu \left(2 \left[\left(\frac{\partial v_r}{\partial r} \right)^2 + \left(\frac{1}{r} \frac{\partial v_\theta}{\partial \theta} + \frac{v_r}{r} \right)^2 + \left(\frac{\partial v_z}{\partial z} \right)^2 \right] + \left[r \frac{\partial}{\partial r} \left(\frac{v_\theta}{r} \right) + \frac{1}{r} \frac{\partial v_r}{\partial \theta} \right]^2 + \left[\frac{1}{r} \frac{\partial v_z}{\partial \theta} + \frac{\partial v_\theta}{\partial z} \right]^2 + \left[\frac{\partial v_r}{\partial z} + \frac{\partial v_z}{\partial r} \right]^2 \right)$$
(IV.4.14)

In the limit of small contact angles, we assume the simple velocity field of Eq. (IV.3.5) It results:

$$\Phi = 12\mu \left(\frac{\frac{dR}{dt}}{R}\right)^2 \tag{IV.4.15}$$

And the total viscous dissipation reads:

$$\frac{dE_v}{dt} = 12\mu V_{drop} \left(\frac{\frac{dR}{dt}}{R}\right)^2$$
(IV.4.16)

Hysteretic dissipation E_h

As the drop spreads or retracts on a non-ideal surface, a part of the total energy of the drop is lost due to the contact angle hysteresis. The hysteretic dissipation for a displacement dR of the contact line reads [115]:

- for an advancing contact line $\left(\frac{dR}{dt} > 0\right)$

$$dE_h = 2\pi R \, sg(dR) \, \gamma(\cos\theta_E - \cos\theta_a) = 2\pi R dR \, \gamma(\cos\theta_E - \cos\theta_a) \quad (\text{IV.4.17})$$

- for a receding contact line $\left(\frac{dR}{dt} < 0\right)$

 $dE_{h} = 2\pi R \, sg(dR) \, \gamma(\cos \theta_{r} - \cos \theta_{E}) = 2\pi R dR \gamma(\cos \theta_{E} - \cos \theta_{r}) \qquad (IV.4.18)$ The contact angle hysteresis (advancing θ_{a} and receding θ_{r}) is either measured or calculated using the model of Raj et al [65] (see chapter I, section I.2.3).

IV.4.3 Harmonic oscillator with solid friction

Our aim is to establish the dynamic equation of a sessile drop when its contact line is mobile. Figure III.3-1b shows that after one oscillation, the drop height is of the order of the equilibrium height H_E , *i.e.* the height of the spherical cap when the contact angle is equal to θ_E . We calculate H_E for the mass of liquid lead used in our experiments ($\rho V_{drop} = 100 \text{ mg}$). It is approximately equal to $H_E \cong 0.5\varepsilon_c$ where ε_c is the critical thickness, *i.e.* the height of a puddle flattened by gravity (see section IV.3). Since H_E is significantly lower than ε_c , the effect of gravity on the drop final shape is negligible. More generally, we will neglect the effect of gravity on the drop dynamics.

The potential energy of the drop is the sum of surface energy and gravitational energy, *i.e.* $E = E_s + E_g$. Since we neglect gravity effects, the drop potential energy reduces to $E = E_s$. The final shape of the drop results from a minimum of potential energy at equilibrium. In absence

of gravity, the equilibrium shape is a spherical cap and its geometric contact angle is equal to the (thermodynamic) equilibrium contact angle.

Under small oscillations assumption, the 2^{nd} order Taylor series expansion of *E* about the equilibrium contact radius R_E reads:

$$E(R) = E_s(R) \cong E_s(R_E) + \left[\frac{dE_s}{dR}\right]_{R=R_E} (R - R_E) + \frac{1}{2} \left[\frac{d^2 E_s}{dR^2}\right]_{R=R_E} (R - R_E)^2$$
(IV.4.19)

We remind that the equilibrium contact radius R_E is the contact radius of the cap when its geometric contact angle is equal to the equilibrium contact angle.

The first derivative of the surface energy with respect to the contact radius reads:

$$\frac{dE_s}{dR} = 2\pi R\gamma(\cos\theta - \cos\theta_E) \tag{IV.4.20}$$

At equilibrium:

$$\left[\frac{dE_s}{dR}\right]_{R=R_E} = 0 \tag{IV.4.21}$$

The second derivative of the surface energy with respect to the contact radius reads:

$$\frac{d^2 E_s}{dR^2} = 2\pi\gamma(\cos\theta - \cos\theta_E) + 2\pi\gamma R \frac{d\cos\theta}{dR}$$
(IV.4.22)

At equilibrium:

$$\left[\frac{d^2 E_s}{dR^2}\right]_{R=R_E} = 2\pi\gamma R_E \left[\frac{d\cos\theta}{dR}\right]_{R=R_E} = 2\pi\gamma \left[\frac{dR}{d\cos\theta}/R\right]_{R=R_E}^{-1}$$
(IV.4.23)

The first derivative of the contact radius with respect to the cosine of the geometric contact angle can be easily calculated from the relationships of the spherical cap reported in section IV.4.1. Figure IV.4-3 presents the variations of $\left(\frac{dR}{d\cos\theta}\right)/R$ as a function of the geometric contact angle of the cap at fixed volume.



Figure IV.4-3: variations of $\left(\frac{dR}{d\cos\theta}\right)/R$ as a function of the geometric contact angle of the spherical cap (at constant volume).

Then:

$$\frac{dE_s}{dt} = 2\pi\gamma R_E \left[\frac{d\cos\theta}{dR}\right]_{R=R_E} (R-R_E)$$
(IV.4.24)

We combine Eqs. (IV.4.19), (IV.4.21), (IV.4.23) and (IV.4.24), we neglect the gravity effects (since $H_E < \varepsilon_c$) and the viscous effects within the liquid (since $Oh \ll 1$) and we obtain the dynamic equation of the oscillating drop with mobile contact line

- when the drop recedes

$$\frac{1}{2}\rho V_{drop}\frac{d^2R}{dt^2} + 2\pi\gamma R_E \left[\frac{d\cos\theta}{dR}\right]_{R=R_E} (R-R_E) + 2\pi R_E\gamma \left(\cos\theta_E - \cos\theta_r\right)$$
(IV.4.25)
= 0

- when the drop advances

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$$\frac{1}{2}\rho V_{drop}\frac{d^2R}{dt^2} + 2\pi\gamma R_E \left[\frac{d\cos\theta}{dR}\right]_{R=R_E} (R-R_E) + 2\pi R_E\gamma \left(\cos\theta_E - \cos\theta_a\right)$$
(IV.4.26)
= 0

This dynamic equation is similar to the equation of a harmonic oscillator with solid friction except that the value of the solid friction coefficient depends on the sign of the contact line velocity.

The pulsation of the harmonic oscillator is given by:

$$\omega_{1} = 2\pi f_{1} = \sqrt{\frac{4\pi\gamma R_{E} \left[\frac{d\cos\theta}{dR}\right]_{R=R_{E}}}{\rho V_{drop}}}$$
(IV.4.27)

This expression slightly differs from the eigenpulsation of large drops flattened by gravity as derived by Noblin et al. [115], i.e.

$$\omega_1 = \sqrt{\frac{16\pi\gamma(1 - \cos\theta_E)}{\rho V_{drop}}}$$
(IV.4.28)

The solid friction coefficient is given by

- when the drop recedes

$$\mu_r = \frac{4\pi R_E \gamma (\cos \theta_r - \cos \theta_E)}{\rho V_{drop}}$$
(IV.4.29)

- when the drop advances

$$\mu_a = \frac{4\pi R_E \gamma(\cos\theta_E - \cos\theta_a)}{\rho V_{drop}} \tag{IV.4.30}$$

Using these parameters, we may rewrite the dynamic equation of the oscillating drop as follows:

$$\ddot{x} + \omega_1^2 x + \mu \, sg(\dot{x}) = 0 \tag{IV.4.31}$$

where $x = R - R_E$, $\mu = \mu_r$ if $sg(\dot{x}) = -1$ and $\mu = \mu_a$ if $sg(\dot{x}) = 1$.

Let make coincide the time origin with the moment when the drop undergoes an oscillation peak. We denote x_0 the position of the contact radius at t = 0 with respect to the equilibrium contact radius.

The contact line motion on time interval $\left[(k-1)\frac{\pi}{\omega_1}; k\frac{\pi}{\omega_1}\right]$ (where k is the number of elapsed half periods since the time origin) is given by

- if k is even

$$x(t) = \left(x_0 - k\left(\frac{\mu_r + \mu_a}{\omega_1^2}\right) + \frac{\mu_a}{\omega_1^2}\right) \cos(\omega_1 t) - (-1)^k \frac{\mu_a}{\omega_1^2}$$
(IV.4.32)

- if k is odd

$$x(t) = \left(x_0 - k\left(\frac{\mu_r + \mu_a}{\omega_1^2}\right) + \frac{\mu_a}{\omega_1^2}\right) \cos(\omega_1 t) - (-1)^k \frac{\mu_r}{\omega_1^2}$$
(IV.4.33)

In order to examine when the oscillator comes to rest permanently, we simply take a unique friction coefficient equal to:

$$\mu = \frac{\mu_r + \mu_a}{2} = \frac{2\pi R_E \gamma (\cos \theta_r - \cos \theta_a)}{\rho V_{drop}}$$
(IV.4.34)

This expression is the same as the one obtained by Noblin et al.[115] for large drops flattened by gravity.

Following Lapidus [119], we define the critical displacement x_c and the factor α :

$$x_c = \frac{\mu}{\omega_1^2} = \alpha x_0 \tag{IV.4.35}$$

 α expresses as

$$\alpha = (\cos \theta_r - \cos \theta_a) \left(\frac{1}{R_E} \left[\frac{dR}{d \cos \theta} \right]_{R=R_E} \right) \left(\frac{x_0}{R_E} \right)^{-1}$$
(IV.4.36)

Then, the position of the contact line is given by:

$$x(t) = x_0 \{ (1 - (2k - 1)\alpha) \cos(\omega_1 t) - (-1)^k \alpha \}$$
(IV.4.37)

We define x_k the position of the contact line at the end of the kth half-period. x_k is given by:

$$x_k = (-1)^k (1 - 2\alpha k) x_0 \tag{IV.4.38}$$

The contact line get permanently stuck at the location x_n when

$$|x_n| \le x_c < |x_{n-1}| \tag{IV.4.39}$$

The number n of half-periods before the contact line immobilization is given by [119]:

$$\frac{1-\alpha}{2\alpha} \le n < \frac{1+\alpha}{2\alpha} \tag{IV.4.40}$$

From Eqs. (IV.4.36) and (IV.4.40), we deduce that the number of oscillations with moving contact line, until the contact line gets permanently stuck, is all the greater when (i) the hysteresis is low, (ii) the equilibrium contact angle is close to 90° (see Figure IV.4-3) and (iii) the initial deviation from equilibrium (x_0/R_E) is large.

Note: We also considered the case where the drop potential energy is not expanded into Taylor series. Then, the model is no more linear and there is no analytical solution. Thus, we implemented this model on Scilab sotfware and solved it using the 4th order Runge-Kutta method (*RK4*). We found that the results of the non-linear model are close to those provided by the linear one.

IV.4.4 Comparison with experiments

Sessile drop natural frequency?

As already mentioned, the sessile drop oscillations with mobile contact line are affected by strong and erratic pinning and depinning events. In order to identify the sessile drop eigenpulsation from this "noisy motion", we performed a spectral analysis of the variations of the contact radius as a function of time using Fast Fourier Transform.

We first determined the eigenfrequency of sessile drops with moving contact line on pure silica surfaces. Figure IV.4-4a shows the variations of the contact line radius as a function of time for a sessile drop on pure silica ($V_0 = 0.55 \text{ m/s}$) and Figure IV.4-4b presents the corresponding periodogram. We note that the periodogram exhibits a predominant peak at 23.42 Hz. This frequency is associated with the oscillations of the sessile drop. Table IV.4-1 reports the frequency of the predominant peak for two samples as well as the theoretical eigenfrequency as calculated by Eq. (IV.4.27). The agreement between the measured values and the theoretical ones is satisfactory (even though the model has been developed under the assumption of small equilibrium contact angle). We note that the agreement is better for the experiment characterized by a greater initial kinetic energy: in that case, the drop undergoes a larger number of oscillations before contact line immobilization.

We then analyzed the contact radius temporal fluctuations of the drops deposited on silicapatterned iron surfaces: the periodograms do not reveal any predominant frequency that could be related to the theoretical eigenfrequency f_1 (as given by Eq. (IV.4.27)). We attributed this result to the characteristic scale of the surface pattern only one or two orders of magnitude smaller than the scale of the drop. We concluded that the present model based on (i) the spherical cap assumption and (ii) a "macroscopic" description of the wetting (Cassie contact angle, advancing and receding angles), is not suitable for the present patterned surface, a "microscopic" description of (i) the surface defects and (ii) the induced contact line distortions is needed.

Hence, we analyzed the experiments of Zaïdi et al. [93] performed on metallic iron partially covered by silicon oxides particles or films (the oxides were obtained after annealing process of binary alloy iron-silicon. In that case, the oxide particles are five orders of magnitude smaller that the drop size. However, the periodograms do not reveal any predominant frequency that could be related to f_1 . We conclude that the model presented in section IV.4.3 is not relevant for sessile drops on chemically heterogeneous surfaces: the advancing and receding contact angles are definitely not sufficient to account for the influence of the surface defects on the sessile drop dynamics when the drop kinetic energy is not large compared to the hysteretic dissipation.

Note: For the experiments carried out on silica-patterned surfaces, the term "oscillation" is abusive since the drop dynamics is not characterized by a predominant frequency. In this case, the term "fluctuation" is more appropriate.



Figure IV.4-4: Contact diameter oscillation on pure silica: (a) signal of the experimental data, (b) periodogram of the signal using the Fast Fourier Transform (FFT).

Table IV	.4-1:	Experimental	and theoretical	eigenfrequencies	of a	sessile drop	with mo	ving line	е
on pure	silica	ι.							

0.1.	V ₀	$ heta_E$	Experimental frequency	Theoretical frequency f_1^{th} (Hz)	
Silica	(m/s)	(°)	f_1^{exp} (Hz)		
Sample 1	0.55	134	23.42	30.8	
Sample 2	0.86	137	28.01	28.9	

Hysteretic dissipation

We theoretically established that the number of oscillations with mobile contact line experienced by a sessile drop before contact line immobilization is related to the parameter α . We remind that α depends on (i) the equilibrium contact angle, (ii) the contact angle hysteresis and (iii) the initial deviation of the contact radius from its equilibrium value.

We counted for each experiment the number of half-oscillations with mobile contact line until the contact line gets permanently stuck. Figure IV.4-5 presents the variations of the experimental number of half-oscillations with moving contact line as a function of $1/\alpha$. The theoretical number of half-oscillations is actually of the order of $1/(2\alpha)$. For our experiments, α is essentially affected by the contact angle hysteresis. The equilibrium contact angle has only a slight effect on α .

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Figure IV.4-5: Number of drop oscillations with mobile contact line (before contact line permanent immobilization) as a function of the dimensionless number α .

We observe that the number of oscillations with mobile contact line on silica patterned surfaces is correlated with the dimensionless number α . However, the number of oscillations decreases with $1/\alpha$ whereas the inverse is theoretically expected.

These discrepancies can be attributed to the strong assumptions of the model. In that respect, the spherical cap assumption impacts the values taken by the dynamic contact angle and therefore the drop dynamics.

We also believe that the dissipation effects are not properly described in the present model: damping seems underestimated for the patterned surfaces with low silica area fractions whereas it seems overestimated for the patterned surfaces characterized by high silica area fractions. The energy losses associated with the pinning and depinning events need to be properly described. We conclude that the present model fails to describe the drop relaxation when its contact line is mobile.

IV.5 Drop oscillations with fixed contact radius

While the drop contact line has stopped permanently, the drop height still fluctuates for a certain time before the drop reaches its final resting state. These fluctuations correspond to the phase (4) of the drop dynamics as defined in section IV.1.

Figure IV.5-1 shows the drop height fluctuations with fixed contact line on four different substrates, i.e. pure iron surface, pure silica surface and two different silica-patterned iron surfaces. We observe that the drop height fluctuations are periodic. In order to precisely determine the frequency of these oscillations, we estimated the power spectrum density (PSD) of the drop height fluctuations as a function of frequency using Fast Fourier Transform (FFT). A typical estimate of the PSD is reported in Figure IV.5-2 for a sessile drop on {100; 100} silica-patterned surface: we note that the periodogram exhibits a predominant peak at 73.85 Hz. This frequency corresponds to the natural frequency of the sessile drop when its contact line is fixed. Table IV.5-1 reports the measured final contact angle θ_f , the measured final contact radius R_f (made dimensionless by R_0) and the frequency f_1^{exp} of the predominant peak as identified by FFT for the different experiments carried out in the present work. It appears that for a liquid lead drop of fixed mass, the sessile drop eigenfrequency increases as the final contact angle decreases, i.e., as the final contact angle decreases, i.e., as the substrate increases.

The oscillations of sessile drops with fixed contact line can be compared to the axisymmetric oscillations of drops partially bound to a rod (Bisch *et al.* [120]) or to a spherical bowl (Strani and Sabetta [121]). Bisch *et al.* [120] studied the case of drops partially bound to a rod, submitted to controlled vibrations and immersed in immiscible liquids of equal density (Figure IV.5-3). They established a simple empirical expression of the mode 1 eigenfrequency f_1 [130; 172]:

$$f_1 = \frac{1}{2\pi} \sqrt{\frac{3K\gamma}{4\pi\rho}} \frac{\sqrt{R}}{R_s^2}$$
(IV.5.1)

where *K* is a constant that should depend on the fluid density ratio (K = 9 for fluids of equal densities). *R* is the contact radius of the drop and R_s is its curvature radius. This law has been validated for R_s/R of 1.3 to 7. We underline that the eigenfrequency of the first mode f_1 scales as R_s^{-2} : it differs from the eigenfrequency of a free drop which scales as $R_s^{-3/2}$ as predicted by

L. Rayleigh [122]. However, the simple equation of Bisch *et al.* cannot be applied to our experiments since the inner to outer fluid density ratio is presently very large, *i.e.*, of the order of 10^4 .

Strani and Sabetta [121] (thereafter noted S&S) theoretically analyzed the linear oscillations of a liquid drop in an outer fluid in partial contact with a spherical bowl under inviscid and zerogravity assumptions (Figure IV.5-3). The calculated mode 1 eigenfrequency f_1 of vibration reads:

$$f_1 = \frac{1}{2\pi} \sqrt{\frac{\gamma}{R_s^3 \rho \lambda_1}} \tag{IV.5.2}$$

with λ_1 the eigenvalue for mode 1 which depends on the geometric contact angle θ and on the phase density ratio. This equation is theoretically valid for arbitrary contact angle and density ratio.

Table IV.5-1 reports the geometric contact angle θ_{cap} that the drop would have if it had the shape of a perfect spherical cap with contact radius R_f , the ratio of the curvature radius to the final contact radius R_s/R_f (where R_s is calculated under the assumption of perfect spherical cap with contact radius R_f) and the theoretical mode 1 eigenfrequency $f_1^{S\&S}$ computed using Strani and Sabetta's model (Eq. (IV.5.2)). As in the work of Bertrandias et al [123], we calculated the first eigenvalue λ_1 using the method of Smithwick and Boulet [124].

Overall, there is a good agreement between the measured and calculated frequencies when the drop is actually in the shape of a spherical cap, i.e. $\theta_{cap} \cong \theta_f$. However, for liquid lead drop on pure silica surfaces, even if $\theta_{cap} \cong \theta_f$ is satisfied, the measured frequencies are significantly lower than the predictions of S&S model. It is not due to a weakness in S&S model since Smithwick and Boulet found a very good agreement between S&S model and the measured eigenfrequencies of mercury droplets on glass surface (contact angle near 130° as for liquid lead on pure silica).

Figure IV.5-4 compares the experimental eigenvalues derived from the experimental eigenfrequencies reported in Table IV.5-1 to the prediction of Strani and Sabetta's model. The lower branch of the curve corresponds to the geometric contact angle lower than 90° and the upper branch to contact angle greater than 90°. As mentioned above, Strani and Sabetta's model does not reflect our experiments for large contact angle values (in particular for silica sample).



Figure IV.5-1: Height oscillations of lead drop on pure substrates and patterned surfaces.



Figure IV.5-2: Periodogram of the drop height oscillations with fixed contact diameter on patterned sample {100; 100} obtained by Fast Fourier Transform (FFT).

Table IV.5-1: Mode 1 eigenfrequency of drop with fixed contact line on pure substrates and patterned surfaces: θ_f is the final contact angle, R_f is the final contact radius, f_1^{exp} is the measured eigenfrequency, θ_{cap} in the contact angle of the perfect spherical cap with contact radius R_f , R_s is the drop curvature radius under spherical cap assumption, $f_1^{S\&S}$ is the theoretical mode 1 eigenfrequency as predicted by Strani and Sabetta's model.

Sample	$ heta_f(^\circ)$	R_f/R_0	$f_1^{exp}(\mathrm{Hz})$	$ heta_{cap}$ (°)	R_s/R_f	$f_1^{S\&S}(\mathrm{Hz})$
Pure iron	55.00	1.69	77.08	53.9	1.24	77.03
{5; 20}	58.13	1.67	67.86	55.4	1.22	77.13
{100; 500}	57.07	1.47	86.96	71.3	1.05	75.58
{100; 500}	70.90	1.47	76.92	71.3	1.05	75.58
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{5;5}	61.78	1.56	79.77	63.8	1.11	76.94
{20; 20}	51.21	1.59	79.84	61.4	1.14	77.15
{20; 20}	49.71	1.29	80	87.3	1.00	69.77
{100; 100}	57.36	1.47	73.85	71.3	1.05	75.58
{100; 100}	54.48	1.11	73.85	104	1.03	61.03
{500; 500}	65.52	1.48	71.86	70.4	1.06	75.78
{500; 500}	61.35	1.47	71.86	71.3	1.05	75.58
{20; 5}	106.32	1.01	61.88	112	1.08	55.67
{20; 5}	103.87	1.09	59.88	105	1.04	59.96
{100; 20}	106.36	1.12	59.88	103	1.02	61.55
{100; 20}	125.26	0.79	55.00	130	1.30	44.36
{500; 100}	103.78	1.00	57.88	113	1.09	55.13
{500; 100}	88.10	1.22	59.88	93.6	1.00	66.61
Pure silica	137	0.78	28.01	131	1.32	43.88
Pure silica	134	0.79	23.42	130	1.3	44.36

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Figure IV.5-3: Drop in partial contact with a spherical bowl as defined by Strani and Sabetta [121], [125].



Figure IV.5-4: First mode eigenvalue: comparison between our experimental data (empty black marks) and the calculations of Strani and Sabetta [121] (*full red lines*).

IV.6 Drop splitting

As already shown, a liquid lead drop retracting on a silica-patterned iron surface undergoes a series of pinning and depinning events on the pure iron stripes. We observed that a strong pinning event may result in the splitting of the drop into several droplets (see Figure IV.1-2). Unexpectedly, drop rupture only occurred on patterned surfaces characterized by low silica area fraction.

The following mechanism is advanced: as the drop is pinned during its retraction, a part of the liquid kinetic energy is "converted" into free surface oscillations. We expect that the drop splits if the amplitude of the vertical oscillations (while the contact line remains pinned) is of the order of the drop height. The lower the silica area fraction, the lower the equilibrium contact angle, the greater the contact radius, the lower the height of the drop. Thus, drop rupture appears more probable on surfaces characterized by low silica area fraction since lower oscillation amplitudes are required. Furthermore, the higher the kinetic energy of the drop, the higher the amplitude of the oscillations when the drop stops. Thus, drop rupture is more probable during the first or the second receding.

In order to substantiate this scenario, we express the vibrational energy required for the drop to split and then compare this energy to the kinetic energy of the drop just before pinning.

IV.6.1 Splitting energy

We are looking for a simple approximation of the splitting energy. We suppose that the pinned drop has a pancake shape. This assumption seems reasonable since drop splitting often occurs early in the receding. In order to determine the vibration modes of a drop with fixed contact radius, we followed the approach of Noblin et al. [115] for a puddle flattened by gravity with immobile contact line.

We first consider the capillary-gravity waves of a liquid bath of height H. If the viscous effects are negligible, the pulsation associated with wave vector q is given by [126]:

$$\omega^{2} = \left(qg + \frac{\gamma}{\rho}q^{3}\right) \tanh qH \tag{IV.6.1}$$

Noblin et al. [115] found that the wavelength associated with the j^{th} vibration mode of a puddle drop satisfies (see Figure IV.6-1):

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$$\left(j - \frac{1}{2}\right)\lambda_j = 2p\tag{IV.6.2}$$

where p is the arc length of the meridian curve from the center to the edge of the drop (when the drop is at rest). If the radius of the drop is large enough compare to its height, a first order approximation of p is given by $p \cong R$ where R is the contact radius.

Then, the wave vector q_j is given by:

$$q_{j} = \frac{2\pi}{\lambda_{j}} \cong \frac{\pi \left(j - \frac{1}{2}\right)}{R}$$
(IV.6.3)

Figure IV.6-1: Effective wavelength for the third mode (j=3) [127].

Noblin et al. found that the eigenpulsations of a puddle drop are actually well described by Eq. (IV.6.1) with *q* satisfying Eq.(IV.6.3).

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If gravitational effects are negligible, the dispersion relation becomes:

$$\omega_j^2 \cong \frac{\gamma}{\rho} \left(\frac{\pi \left(j - \frac{1}{2} \right)}{R} \right)^3 tanh \frac{\pi H \left(j - \frac{1}{2} \right)}{R}$$
(IV.6.4)

where H would be the height of the drop if it was at rest with contact radius R.

The peak vibrational energy associated with mode *j* reads:

$$E_j = \frac{1}{2} \rho V_{drop} \omega_j^2 A^2 \tag{IV.6.5}$$

where *A* is the amplitude of the vibrations. Splitting occurs when $A \cong H$. Then, the splitting energy when the *j*th mode is excited, reads:

$$E_{split} \cong \frac{1}{2} \rho V_{drop} \omega_j^2 H^2 = \frac{1}{2} \gamma H^2 V_{drop} \left(\frac{\pi \left(j - \frac{1}{2} \right)}{p} \right)^3 tanh \frac{\pi H \left(j - \frac{1}{2} \right)}{R}$$
(IV.6.6)

We consider the second mode (j = 2) since in that case, splitting energy is minimal.

Under puddle approximation, the height of the drop is:

$$E_{split} \approx \frac{1}{2} \rho V_{drop} \omega_j^2 H^2 = \frac{1}{2} \gamma H^2 V_{drop} \left(\frac{\pi \left(j - \frac{1}{2} \right)}{p} \right)^3 tanh \frac{\pi H \left(j - \frac{1}{2} \right)}{R}$$
(IV.6.7)
$$H = \frac{V_{drop}}{\pi R^2}$$
(IV.6.8)

So the minimal splitting energy is given by:

$$E_{split} \cong \frac{27}{16} \pi \gamma \frac{V_{drop}^3}{R^7} \tanh \frac{3V_{drop}}{2R^3}$$
(IV.6.9)

We emphasize that Eq.(IV.6.9) is a rough estimate of the splitting energy since splitting typically occurs for large oscillations, when the regime is most likely non-linear.

IV.6.2 Kinetic energy of the drop

Under puddle assumption, the kinetic energy of the drop reads (section IV.3)

$$E_c \simeq \frac{1}{4} \rho V_{drop} \left(\frac{dR}{dt}\right)^2 \tag{IV.6.10}$$

Splitting criterion

We expect the drop to split into droplets if the two following conditions are together satisfied:

- (i) The drop contact line is strongly pinned
- (ii) The energetic criterion is satisfied: the energy ratio is greater than 1 just before pinning, i.e. $\frac{E_c(t_0^-)}{E_{split}(t_0^-)} > 1$ if pinning occurred at t_0 .

IV.6.3 Application of the model

To verify if the splitting criterion defined above is relevant, we select four samples from our experimental data:

- Two samples of patterned surfaces where splitting never occurred: {20; 5} and {20; 20}
- Two samples of $\{5; 20\}$ where splitting may occur.

In Figure IV.6-2, for the patterned surfaces {20; 5} and {20; 20}, we can see that the energetic criterion is never satisfied when the drops get pinned: the energy ratio is systematically much lower than 1 just prior to the pinning events.

On the contrary, on patterned surfaces {5; 20}, the energetic criterion is satisfied just before the first pinning events. According to the defined splitting criterion, the drop should split in both experiments. Nevertheless, the drop splits only in the second one. Indeed, in the present experiments, we do not control the way the vibrational modes are excited when the drop gets pinned. However, these aspects also condition the breaking or the non-breaking of the drop.

We conclude that the above criterion only informs us about the risk that the drop splits on a given patterned surface. We expect that the higher the energetic criterion, the higher the probability that the drop will split.







Figure IV.6-2: Ratio of drop kinetic energy to theoretical splitting energy. (a) and (b): patterned surfaces where drop splitting never occurred. (c) two samples of {5; 20} patterned surface: drop splits in (d) but does not in (c).

IV.7 Conclusion

In this chapter, we examined the different phases of the sessile drop dynamics, i.e. from the initial spreading upon impact until the final resting state. When it was relevant, we applied analytical models already available in the literature. Otherwise, we developed our own models.

The values of the Weber and Ohnesorge numbers characterizing the drop impact states that the spreading is *impact driven*: the droplet spreading is mainly driven by the impact velocity and the spreading resistance is due to inertia. Thus the spreading timescale is the inertial time defined by $t_i = D_0/V_0$.

To account for the substrate wettability, we introduced a modified Weber number $We' = We/(1 - \cos \theta_E)$ and a modified impact parameter $P_I = We'/Re^{\frac{2}{5}}$. Our data are located in a P_I range where the initial spreading is not solely controlled by inertia and capillarity. It is also affected by viscous effects. Consistently we found that the maximal spreading diameter is well described by Clanet et al. scaling law, i.e. $D_{max}/D_0 \propto We'^{1/4}$.

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During this phase, the spreading diameter evolves as the square root of time:

$$\frac{D(t)}{D_0} = \alpha_2 \left(\frac{t}{t_i}\right)^{1/2} \tag{IV.7.1}$$

where α_2 depends on the modified Weber number.

The spreading phase is followed by the receding phase. The timescale at the beginning of the first receding is the inertial capillary time given by:

$$\tau_r = \sqrt{\frac{\pi \rho V_{drop}}{\gamma (1 - \cos \theta_r)}}$$
(IV.7.2)

And the contact radius of the receding drop is well described by:

$$\frac{R}{R_{max}} = \cos\left(\sqrt{\frac{4\pi\gamma(1-\cos\theta_r)}{\rho V_{drop}}}t\right)$$
(IV.7.3)

This law holds only at the beginning of the receding.

When a liquid lead drop further retracts on a silica patterned iron surface, it undergoes a series of pinning and depinning events on the pure iron stripes. In a few cases, a strong pinning event may result in the splitting of the drop into several droplets. Indeed, as a drop is pinned during its receding, its kinetic energy is partially converted into free surface oscillations. If the potential energy associated with these oscillations exceeds a certain threshold, the drop splits. The minimum energy required by the drop (of contact radius R) to divide was estimated at:

$$E_{split} \cong \frac{27}{16} \pi \gamma \frac{V_{drop}^3}{R^7} tanh \frac{3V_{drop}}{2R^3}$$
(IV.7.4)

In most cases, the drop remains whole and relaxes as it is until rest. At the beginning of the relaxation, the drop oscillates with a stick-slip motion of the contact line. Finally, the contact line stops permanently and the drop oscillates with fixed contact line until resting state.

We established a simple analytical model of oscillating drop with moving contact line. This model accounts for the mode 1 eigenfrequency of drops deposited on pure silica surfaces but it fails to describe the drop behavior on silica patterned surfaces. Indeed, the pinning and depinning events on the silica pillars are very dissipative and strongly affects the drop dynamics. The contact angle hysteresis only partially reflects these phenomena. They need to be described in more detail and require a modelling at the scale of the silica pillars.

Last, the drop oscillations with fixed contact line are well described by Strani and Sabetta's model (S&S) originally established for a drop bound to a spherical bowl: the measured mode 1 eigenfrequencies are in good agreement with the prediction of S&S model.

Note: Figure IV.7-1 compares the mode 1 eigenfrequency of a drop (of volume V_{drop}) with moving contact line (our model), the mode 1 eigenfrequency of a drop with fixed contact line (as given by S&S model), and the eigenfrequency of a free drop of double volume ($2 \times V_{drop}$). The latter frequency is identical to the eigenfrequency of a hemispherical sessile drop (of half volume, i.e. V_{drop}) with a free contact line and a fixed contact angle equal to 90°. This frequency may be calculated from Lamb [128]

$$\omega_n = 2\pi f_n = \sqrt{\frac{(n-1)n(n+1)(n+2)\gamma}{(\rho(n+1) + \rho_c n)R^3}}$$
(IV.7.5)

with n = 2 and the density of the continuous phase $\rho_c \approx 0$.

We observe that the variations of the eigenfrequency of the drop with free contact line are similar to the variations of the eigenfrequency provided by S&S model. Consistently, for the same curvature radius to contact radius ratio, the eigenfrequency of the drop with moving contact line is lower than the eigenfrequency with fixed contact line (S&S). We note that for $R_s/R = 1$ ($\theta_E = 90^\circ$), the eigenfrequency of our model lies between S&S eigenfrequency and the eigenfrequency of a hemispherical sessile drop with free contact line and fixed contact angle.

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Figure IV.7-1: Comparison of the different eigenfrequencies. Drop oscillation with a moving contact line (blue line), drop oscillation with a fixed contact line (red line), free drop oscillation (the cross mark)

Conclusion and perspective

This work is a contribution to a better understanding of the wettability of heterogeneous ironoxide surfaces by liquid metals. It is devoted to the study of the influence of oxides during physical wetting and then bring a better understanding of the steel sheet wettability during galvanization process. In fact, since the oxides formed on industrial steel sheets do not allow a good wetting of the steel sheet, it is essential to understand the wetting phenomena of heterogeneous iron-oxide surfaces. However, most of the wettability studies were carried out on iron alloys after annealing. During this annealing process, addition elements such as silicon and manganese diffuse to the surface by selective oxidation to form particles or films. These oxides are generally of different shapes, sizes and distribution and then do not allow a detailed study.

To answer this problem, we used iron-silica textured surfaces. These surfaces were designed by plasma-enhanced chemical vapour deposition followed by photolithographic process. That allow to made heterogeneous surfaces with square silica of size and inter-distance between 5 μ m and 500 μ m. In addition to these textured surfaces, we also used pure iron and silica substrates as a reference for the study of textured surfaces. Then, we studied the wetting of heterogeneous iron-oxide surfaces from 0% to 100% of oxide covering rate.

On the other hand, we used lead as a metal, instead of a zinc alloy. Indeed, the wetting of these heterogeneous iron-silica surfaces by zinc is reactive and modifies the liquid solid interface. This brings a new complexity to the study of wetting. The choice of lead allowed to study only the physical (non-reactive) wetting of the textured surfaces.

The wetting experiments were carried out using the dispensed drop technique. First, the textured surfaces are annealed at high temperature in a reducing atmosphere (N₂- 5 vol. % H₂) to reduce surface iron oxides. Then, the drop is dispensed to the surface and spreads on it. This was filmed and recorded using a high-resolution and high-speed camera at 1000 frames/second. Then, we implemented image analysis techniques to characterize the wetting. These techniques allow to measure the three main wetting parameters: diameter and height of the drop and its contact angle. On the solidified drop, the circularity criterion of the drop contact on the patterned surface was estimated and the triple contact line was positioned with respect to the patterns, on as many samples as possible. From these experimental studies, different results were obtained.

Experimental results

First, after the impact, the drop spreads to its maximum spreading diameter. This phase is called the spreading phase. It is followed by the first receding phase. Then two cases of drop behaviour were observed, depending on the silica area fraction. In the first case, the drop continues its receding before oscillating until its final state. This first case is most common on patterned surfaces with high silica area fraction (25%, 64% and 70%). In the second case, the drop is retained during its receding: stick-slip motion. This is most frequently encountered on surfaces with low silica coverage rates (3% and 4%). In some cases, the stick-slip motion leads to the split of the drop into several pieces.

Then, stick-slip motion phenomenon leads to a deformation of the drop shape on the patterned surface. Image processing and scanning electron microscopy (SEM) showed that the triple contact line is mainly on pure iron, by bypassing silica patterns.

The influence on the wetting of the spreading direction of the triple contact line in relation to the patterns was negligible. However, when the drop is strongly deformed, it is more elongated in direction d1 (parallel to the sides of the square patterns) than in direction d2 (parallel to the diagonal of the square patterns). In addition, we showed that the solidification of the drop does not change the spreading diameter and contact angle measured of the drop.

On the influence of pattern size and distribution, we showed it is negligible on the wetting. In fact, the average dynamic of the drop spreading is very close on textured surfaces with the same silica fraction. This is true regardless of the size of the oxides and their distribution. Very few differences were also observed on the solidified drop, depending on the spreading direction. Differences were observed only from one silica surface fraction to another.

This led us to the influence of the area fraction covered by silica on the final contact angle and on the contact angle hysteresis. Due to the stick-slip motion, the final contact angle of the drop on samples with low and moderate silica area fraction is close to a receding contact angle. The final angle only increases on surfaces with high silica area fraction.

Consequently, we showed that the surface fraction of oxides plays a key role in wetting, contrary to their size and distribution.

We also showed that the receding contact angle (minimum angle during drop receding) is almost constant on all textured surfaces regardless of the silica surface fraction. These results are in agreement with those obtained by other authors in literature [14], [15], [65].

Modelling of the spreading dynamics

We examined the different phases of the sessile drop dynamics, i.e. from the initial spreading upon impact until the final resting state.

First, the values of the Weber and Ohnesorge numbers characterizing the drop impact states that the spreading is *impact driven*: the droplet spreading is mainly driven by the impact velocity and the spreading resistance is due to inertia. To account for the substrate wettability, we introduced a modified Weber number $We' = We/(1 - \cos \theta_E)$ and a modified impact parameter $P_I = We'/Re^{\frac{2}{5}}$. Our data are located in a P_I range where the initial spreading is not solely controlled by inertia and capillarity. It is also affected by viscous effects. Consistently we found that the maximal spreading diameter is well described by Clanet et al. scaling law, i.e. $D_{max}/D_0 \propto We'^{1/4}$. During this phase, the spreading diameter evolves as the square root of time.

At maximum spreading, the drop is out of thermodynamic equilibrium. Then, the spreading phase is followed by the receding phase. We showed that the timescale at the beginning of the first receding is the inertial capillary time τ_r . We proposed a macroscopic model which well describes the contact radius of the receding drop until about $0.1\tau_r$. Beyond, the spreading dynamics undergo series of pinning and depinning events on the pure iron stripes.

On iron-silica patterned surfaces with low silica area fraction, a strong pinning event may result in the splitting of the drop into several droplets. This splitting was studied and we proposed a criterion based involved energies: the kinetic energy which is partially converted into free surface oscillations and the potential energy associated with these oscillations.

On iron-silica patterned surfaces with low and high silica area fraction, the drop remains whole and relaxes as it is until rest. First, the drop oscillation is damped by stick-slip motion of the contact line. Then, the contact line remains constant but the drop continues to oscillate with fixed contact line until resting state.

We established a simple analytical model of oscillating drop with moving contact line. This model successfully describes the mode 1 eigenfrequency of drops deposited on pure silica surfaces but not on silica patterned surfaces. Indeed, the pinning and depinning events on the silica pillars are very dissipative and strongly affects the drop dynamics.

Finally, we showed that the drop oscillations with fixed contact line are well described by Strani and Sabetta's model (S&S) originally established for a drop bound to a spherical bowl: the measured mode 1 eigenfrequencies are in good agreement with the prediction of S&S model.

Perspective

In addition to this thesis work, some axes of reflection may be considered. They could be divided into 3 main areas:

Textured surfaces

We used ten textures with patterned sizes between 5 μ m to 500 μ m, in addition to pure substrates. The surface fractions of oxides were as follow: 0%, 3%, 4%, 25%, 25%, 64%, 70% and 100%. It would be interesting to complete this study with textured surfaces of oxide area fraction around 10% and 40%. This would complete the influence of the oxide area fraction on the final contact angle and contact angle hysteresis.

Furthermore, another initial objective of this work was to study the wetting transition: from wetting of liquid metal in base contact with the heterogeneous surface (Wenzel state) to the wetting of liquid with gas under the drop. This is in order to study the critical size of the oxides from which gas is trapped under the drop. Diawara [2], in his work, was able to study this wetting transition on alloy sample Fe-Si, after annealing. However, this wetting transition was not observed on the textured surfaces studied in this work, given the low height of the silica patterns ($h/d \sim 0$) in accordance with the results of the literature. To be able to study such wetting transition surfaces with an h/d ratio greater than 1 are required.

Contact angle hysteresis

In this work, contact angle hysteresis was estimated from the spreading dynamics. However, the speed of this spreading does not allow a better estimation of the contact angle hysteresis. It would be interesting to measure contact angle hysteresis on our textured surfaces using more appropriate techniques such as the sandwich drop method.

Modelling of the spreading dynamics

The spreading dynamics of the lead drop on iron-silica patterned surfaces are subject to pinning and depinning effects. We have not been able to model these phenomena in this work. Indeed, the scales involved (size of the plots compared to the drop size), the texturing of the surface and the spreading velocity require a more precise modelling at the scale of the silica pillars. Given the impact of these phenomena on spreading, it would be interesting to be able to model these phenomena.

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Appendices

A Dimensional analysis

A.1.Static apparent contact angle.

The variables involved to account for the apparent static contact angle θ^* are θ_{YS} , γ_{LV} , ρ , g, h, d, s and R the characteristic dimension of the liquid drop. The systems considered here can therefore be described by nine physical variables, two of them being non-dimensional (θ^* , θ_{YS}), the seven others being expressed by three physical dimensions (kg, m, s). From the Buckingham π theorem, it can be deduced that these systems are described by six non-dimensional numbers.

Two of them are the apparent and Young contact angles (θ^* , θ_{YS}).

The patterned surfaces under investigation are characterized by the Wenzel's roughness and the surface area fraction of the pillar tops. r_W and f_S are function of two dimensionless parameters: $\frac{s}{d}$ and $\frac{h}{d}$.

The characteristic dimension *R* of the liquid drop can be compared to the distance *s* between the pillars. In the systems under investigation, the liquid drop is much larger than the dimensions of the texture. If *R* were of the same order of magnitude as $s, \frac{R}{s}$ should be taken into account.

The apparent contact angle is linked to the wetting of the solid by the liquid. The penetration of the liquid inside the asperities of the solid can be enhanced when the size of the drop is increased. In other words, what is the influence of the hydrostatic pressure of the drop compared to the wetting properties of the system. Bico [9] proposed a simple model for a solid composed of cylindrical pillars in a square distribution.

This model is tailored here to square pillars in a square distribution. Let's consider a spherical liquid drop ($R \ll \kappa^{-1}$) resting on a patterned solid. It is assumed that air remains trapped in the texture under the drop. The contact between the solid and the liquid is a disk of radius r_c (Figure A1.1).

$r_{\rm C} = R \sin \theta^* \tag{A.1}$

When the solid is not wetted by the liquid, $r_C \ll R$ and the volume of the liquid drop is about the volume of a sphere of radius *R*.



Figure A1.1. A spherical liquid drop resting on a patterned solid

The surface area fraction of the pillar tops is given by:

$$f_S = nd^2 \tag{A.2}$$

where n is the number of pillars per unit surface area.

The drop is in contact with $n\pi r_c^2$ pillars and the weight applied to one pillar is given by:

$$P = \frac{4R^3\rho g}{3nr_c^2} \tag{A.3}$$

The drop is maintained at the top of the pillars provided that:

$$4d\gamma_{LV}|\cos\theta_{YS}| > \frac{4R^3\rho g}{3nr_c^2} \tag{A.4}$$

Or

$$\frac{Rd}{\kappa^{-2}} < 3f_S \sin^2 \theta^* |\cos \theta_{YS}| \tag{A.5}$$

with $sin^2\theta^* = 1 - cos^2\theta^*$ and $cos\theta^* = f_S cos\theta_{YS} - 1 + f_S$.

In most of the cases reviewed here, this inequality is verified, meaning that the influence of the dimensionless number $\frac{Rd}{\kappa^{-2}}$ can be neglected.

B More information on the transition from the Cassie regime to the Wenzel regime

B.1. Metastable states



Figure B.1: Definitions of parameters for a textured square pillars in a square arrangement [35].

The Cassie state is often observed even if the condition given by Eq. (I.2.10) is not fulfilled. It means that the Cassie state might be metastable, i.e., exist instead of the stable Wenzel state. The metastable Cassie state is shown in Figure I.2-3 with the dotted line.

The first condition permitting air entrapment under the drop is to obtain the Young contact angle at the different horizontal contact lines (with air trapped below). This condition can be achieved only if the local solid slopes are large enough. It means that there is a transition from the Wenzel to the Cassie regime when the roughness is increased. From Eq. (I.2.9),

$$r_W > f_S + \frac{f_S - 1}{\cos\theta_{VS}} \tag{B.1}$$

Generally, the Young contact angle cannot be obtained for a crenelated solid. In this case, the existence of air / liquid interfaces below the drop is due to the pinning of the triple line on the edges of the spikes, leading to a metastable Cassie state [7].

[56], [57] also showed the existence of mixed Wenzel-Cassie state, i.e. the drop permeates the surface texture without touching the bottom and trapping some air pockets. In this situation, the measured contact angles are stronger than those predicted by the Wenzel relation due to the emergence of a mixed system between the regimes of Wenzel and Cassie.

B.2. Thermodynamic energy barrier

The thermodynamic energy barrier of a smoothly deposited drop on textured can be calculated from the total free surface energy of the system [55]:



Figure B.2: A smoothly deposited drop on pillar textured surfaces [55].

Then, depending on the regime (Cassie or Wenzel states), the total free surface energy of the system can be written:

$$E_{surf}(x, y, \theta) = \gamma_{LV} S_{ext} + c(x, y, \theta) S_{base} + r_W \gamma_{SV} S_{total}$$
(B.3)

Where $c(x, y, \theta)$ depends on the wetting regime. In the Cassie regime (drop suspended on the pillar tops),

$$c(x, y, \theta) = C_{comp} = -\gamma_{LV} \left[f_S \left(1 + \frac{4dx}{a^2} \right) \cos \theta_Y + (1 - f_S) y \right]$$
(B.4)

And in the Wenzel state, $c(x, y, \theta) = C_{wet} = -\gamma_{LV} r_W \cos \theta_Y$

$$E_{surf}(x, y, \theta) = \pi \left(\frac{3V}{\pi}\right)^{2/3}$$

$$\times \frac{1}{(2 - 3\cos\theta + \cos^3\theta)^{2/3}} \left[2\gamma_{LV}(1 - \cos\theta) + c(x, y, \theta)\sin^2\theta\right]$$

$$+ r_W \gamma_{SV} S_{total}$$
(B.5)

Of course, the minimization of this energy gives the classical laws of Cassie and Wenzel.

Moving from the Cassie state to the thermodynamic favoured Wenzel state requires that an energy barrier to overcome, due to the filling of the asperities with liquid. This energy barrier can be approximated to the differential energy in the Cassie (x = 0) state and the hypothetical Wenzel state corresponding to the Cassie state with x = h (non-composite state) at constant contact angle.
$$\Delta E_{barrier} = E^{comp}_{surf} (x = 0, y, \theta_{comp}) - E^{comp}_{surf} (x = h, y, \theta_{comp})$$
(B.6)

With

$$\cos\theta_{comp} = f_S \cos\theta_Y + (1 - f_S)y \tag{B.7}$$

Thus, the transition occurs at lower energy barrier or when the drop vibration energy balances is sufficiently large to balance this energy barrier [55].

B.3. Model based on drop pressure

A drop of volume V_L deposited on horizontal surface exercises on it a pressure P_i , called internal drop pressure obtained from gravity and given by:

$$P_i = \frac{V_L \rho g}{\pi (R(\theta))^2} , \qquad R(\theta) = \left[\frac{6V}{\pi (1 - \cos\theta)(3\sin^2\theta + (1 - \cos\theta)^2)}\right]^{1/3}$$
(B.8)

Where $R(\theta)$ is the radius of the droplet in contact with the surface of apparent contact angle θ .

Assuming the drop to be sufficiently small, the weight of the suspended drop F_w is given by:

$$F_w = \rho g V_u \tag{B.9}$$

The volume of the suspended drop (or unsupported drop) V_u is: $V_u = V_L - f_s h_d A$, where the liquid drop has a density of ρ , a total volume of V_L , a height of h_d with apparent contact area A and a surface tension of γ .

According to Extrand studies [12], [35], to suspend a drop on a textured surface, three conditions must be satisfied:

- 1. The interaction of a drop with the roughness solid at the contact line must direct surface forces upward, i.e. $\theta_Y > 90^\circ$, contrary to the some experimental results in literature [56], [73] where hydrophocity has been reached with homogeneous textured hydrophilic surface NOA. In our case, we will consider this condition always satisfied since we will deal with hydrophobic surfaces.
- 2. Surface forces must be able to maintain the drop against downward forces that favour drop drooping such as gravity called "contact line density criterion".
- 3. The asperities should be higher than liquid protruding between the more distant successive pillars called "pillar height criterion".

If the surface is a homogeneous textured surface as in Figure I.2-4, the contact line density Λ is defined by the relation:

$$\Lambda = \frac{4d}{(s+d)^2} \tag{B.10}$$

We will notice by s_{amax} as greatest linear distance between adjacent pillars: $2s_{amax} = \sqrt{2} s$, the advancing, receding and equilibrium contact angles on the smooth surface by $\theta_{a,0}$ and $\theta_{r,0}$, respectively, and θ_a and θ_r respectively the advancing and receding apparent contact angles on the textured surface.

- Contact line density criterion

The surface forces *F* exerted by the surface to the drop depend on the surface tension γ , the contact angle and the surface of solid-liquid contact area *A*:

$$F = 4d\alpha_a A \gamma \cos(\theta_{a,0} + \omega - 90^\circ)$$
(B.11)

With α_a the area density of the asperities: $\alpha_a = \frac{1}{(s+d)^2}$.

At the equilibrium, these two forces are equal, then we can obtain the critical value of the density contact line Λ_c :

$$\Lambda_{c} = -\frac{\rho g V \left(1 - \frac{\alpha_{p} h_{l} A}{V}\right)}{A \gamma \cos(\theta_{a,0} + \omega - 90^{\circ})}$$
(B.12)

If the drop is small enough, it retains spherical proportions, and in this condition, it can been demonstrated from simple trigonometric calculations:

$$h_{d} = \left[\frac{3V}{\pi} \times \frac{1 - \cos\theta_{a}}{2 + \cos\theta_{a}}\right]^{1/3} , A$$

$$= \pi^{1/3} (6V)^{2/3} \left[\tan(\frac{\theta_{a}}{2}) \times \left(3 + \tan^{2}\frac{\theta_{a}}{2}\right) \right]^{-2/8}$$
(B.13)

Thus, the critical value of the contact line density becomes:

$$\Lambda_{c} = -\rho g V^{\frac{1}{3}} (1 - k_{corr}) \frac{\left[tan\left(\frac{\theta_{a}}{2}\right) \times \left(3 + tan^{2}\frac{\theta_{a}}{2}\right) \right]^{\frac{2}{3}}}{(36 \times \pi)^{\frac{1}{3}} \gamma \cos(\theta_{a,0} + \omega - 90^{\circ})}$$
(B.14)

Where k_{corr} is a correction factor which is equal to zero pour small α_a and for high apparent contact angle θ_a :

$$k_{corr} = \alpha_a \left(\frac{96(1 - \cos\theta_a)}{2 + \cos\theta_a}\right)^{1/3} \times \left[\tan(\frac{\theta_a}{2}) \times \left(3 + \tan^2\frac{\theta_a}{2}\right)\right]^{-2/3}$$
(B.15)

The drop is suspended on the top of pillars, if $\Lambda > \Lambda_c$. Then at the transition point $\Lambda = \Lambda_c$, equations give the dimensionless critical distance between pillars $\left(\frac{s}{d}\right)_c$ beyond which the wetting regime will switch from Cassie to Wenzel states.

$$\left(\frac{s}{d}\right)_c = \left(\frac{4}{\Lambda_c \times d}\right)^{1/2} - 1 \tag{B.16}$$

This last relation shows that for a given critical line density, the dimensionless critical distance depends on the pillar size and it is as great as the pillar size is smaller.

Other authors have found analogical results [56], [57], where the critical pressure P_c of the Cassie regime which is the maximum possible pressure of the drop to be maintained on the pillar top is inversely proportional to pillar size for a given Cassie fraction.

$$P_c = \frac{4\gamma f_s \cos\theta_Y}{(1 - f_s)d} \tag{B.17}$$

But this analysis is only valid if the pillar height has no effect on the transition regime (pillar height sufficiently large).

- Pillar height criterion

When one deposits a liquid on textured surfaces, the liquid can protrude downward between successive pillars (in order to locally respect Young relation on asperity sides). That creates a drop extension of diameter δ_p (or protrusion depth), depending on the contact angle and the distance between pillars:

$$\delta_p = s_{amax} tan\left(\frac{\theta_{a,0} + \omega - 180}{2}\right) \tag{B.18}$$

Thus, the drop will still maintained on the top of pillar if the protrusion depth d is less than the pillar height $h: h > \delta_p$ with a transition point expression:

$$\left(\frac{h}{d}\right)_{c} = \sqrt{2} \times tan\left(\frac{\theta_{a,0} + \omega - 180}{2}\right) \times \frac{s}{a}$$
(B.19)

Finally, the drop is suspended as long as the two criteria are verified. This model has been successfully applied to several experimental results [17][29][30][129].

C Patterned surfaces: comparison with published models

In this part, the experimental points extracted from the literature for textured surfaces (section I.3) are compared to the different models presented in section I.2: Cassie's and Wenzel's laws for the equilibrium contact angle, the wetting transition and the model of Raj et al. [69] for the contact angle hysteresis.

C.1.Equilibrium contact angle

We are interested here in the contact angles obtained at low temperature for homogeneous textured surfaces that were collected in Table I.3-1 and Table I.3-2. In Figure C.1, the advancing, receding and equilibrium contact angles are plotted together with the evolution of Wenzel's and Cassie's laws as a function of s/d (Figure top) and h/d (Figure bottom). In this case, as explained above, air can be trapped under the droplet and, for this reason, the contact angle is estimated with Cassie's law for an air/solid composite surface.

As expected, the equilibrium contact angle, estimated with Wenzel's and Cassie's laws, is located between the corresponding advancing and receding contact angles in the ranges of s/d and h/d investigated.

The value of the theoretical angle is closer to the advancing and equilibrium contact angles than to the receding contact angle. Wenzel's and Cassie's laws are qualitatively consistent with the main observations obtained for the advancing and equilibrium contact angles, namely the evolution of θ_a , θ_{eq} when s/d or h/d is increased.



Figure C.1: Equilibrium (*), advancing (\bullet) and receding (O) contact angles as a function of the dimensionless lengths s/d (top) and h/d (bottom). Comparison with the Wenzel and Cassie models [67]–[69],[70], [72], [74].

C.2.Wetting transition

Figure C.2 shows the experimental transition for the collected data. This is compared to the transition predicted by Wenzel and Cassie in Eq. (I.2.12). Note that, we built the map of Figure C-2 by taking the transition obtained on the evolution of the advancing contact angle.

The theoretical transition predicted with Wenzel and Cassie's laws (solid line in Figure C.2) does not correspond to the experimental transition (dotted line) and therefore does not predict the wetting transition quite well. This means that thermodynamic equilibrium is generally not achieved for composite surfaces. In fact, the figure shows that, for a given dimensionless height $\frac{h}{d}$, the transition from Cassie to Wenzel regimes occurs for a dimensionless spacing $\frac{s}{d}$ higher than the one predicted by the models. And for a given dimensionless spacing, the transition from the Cassie regime to the Wenzel regime occurs at a lower dimensionless height. Thus, surface hydrophobicity tends to favour the metastable Cassie regime [13] or a mixed Cassie and Wenzel states [56], [83], by the entrapment of air pockets under the drop.



Figure C.2: Wenzel (•) *and Cassie* (•) *states as a function of h/d and s/d, liquid metal case in red. Experimental transition (dotted line), theoretical Wenzel / Cassie transition (black solid line), data collected from references* [14], [15], [23], [55], [56], [66]–[70], [72]–[75], [77].

Comparison with models

The energy barrier of the transition from Cassie to Wenzel state can be estimated from thermodynamic study of the liquid-solid system. Figure C-3 shows the evolution of this energy barrier in function of dimensionless pillar distance (s/d) and for each pillar size *d*, showing that the minimum of the energy barrier falls at smaller ratio (s/d) when *d* is higher. Then, one can calculate for each pillar size the corresponding $\left(\frac{s}{d}\right)_c$ beyond which the drop will fall to the Wenzel state from Cassie one.



Figure C-3: Energy barrier with h/d=3, $\theta_Y = 105$ as function of dimensionless pillar distance s/d for a given pillar size. The minima of the energy barriers are marked by X.

The two (Energy barrier and Extrand) models are compared to some experimental literature data, in Figure C.4. The two model's predictions are very similar and there is a right sense of the transition. In these models, energies and forces balances are used which are known to be interchangeable. Also, a quantitative agreement with experimental data is found.



Figure C.4: Wenzel (•) and Cassie (•) states as a function of d and s/d, thermodynamic energy barrier model [55] (red dotted line), model of Extrand [58] (blue dotted line). With h/d=3, $\theta_Y = 105$, $\theta_{a0} = 120$ and $\theta_a = 155$. Data collected from references [23], [55], [56], [69]–[72], [75], [77].

At a given high pillar height (h=60 µm, in our calculation), one can compute from Extrand density criterion and the thermodynamic energy barrier, the transition in $\{\left(\frac{h}{d}\right)_{eq}, \left(\frac{s}{d}\right)_{eq}\}$ plan, in

Figure C.5.

The minimum value of the dimensionless height of pillar (around 0.4) for entrapping air beneath the drop is not predicted by the two models. But the height criterion is expected to predict the transition at moderate pillar height where the transition is very sensitive to the pillar height. At large pillar height, one can expect the transition independent on pillar height and only be controlled by the balance between surface energy and the exerted pressure by the drop or by the energy barrier. In this case the model of Extrand [58]) and the thermodynamic energy barrier model well apply.



Figure C.5: Wenzel (•) and Cassie (•) states as a function of h/d and s/d, metal liquids case in red. Experimental transition (black dotted line), theoretical Wenzel / Cassie transition (black solid line), Extrand [58] height criterion (blue solid line) and density criterion (blue dotted line), thermodynamic barrier model[55]. Data collected from references [14], [15], [23], [55], [56], [66]–[70], [72]–[75], [77]

However, these models are very sensitive to the contact angles and drop volume. For instance, a small variation on the advancing contact angle induces large deviation on the predicted transition (Figure C.6).



Figure C-6: Contact angle influence on thermodynamic energy barrier model (dotted line), Extrand model (dotted line). For $\theta_a = 100^{\circ}(black)$, $\theta_a = 120^{\circ}(blue)$, $\theta_a = 130^{\circ}(red)$ with h/d=3.

C.3. Contact angle hysteresis

As described in section I.2.3, the so called "Cassie on line" relations with the local line fraction factors along TCL have successfully predicted some experimental data [21], [62], [65], [74], [130]. One can compare some of them to the collected literature experimental data. In the composite regime (Cassie regime), the solid interconnectivity governs the hysteresis. It is well known that when the more wetting defects are interconnected then the receding contact angle is nearly constant and only the advancing one changes in function of Cassie fraction or the linear fraction along the TCL (Figure C.7). For our collected data (super-hydrophobic textured surfaces), it is the less wetting defect (air) which is interconnected, then the advancing contact angle is nearly constant as shown in Figure I.3-1 and only the receding angle undergoes a notable variation.



Figure C.7: Contact angle hysteresis in function of the Maximum pillar fraction of a nondistorted TCL. Receding angle (empty mark) and advancing contact angle (full mark). Data collected from references [69] (•), [73] (•), [67] (•), [70] (•), [23] (•), [77] (•).

Depending on the texture and the used experimental method, the drop will be pinned differently. In the "Cassie on line" models, the receding contact angle on a composite surface can be written as:

$$\cos \theta_r = f_{eff} \cos \theta_{r1} + (1 - f_{eff}) \cos \theta_{r2} \tag{C.6}$$

Where f_{eff} is the effective fraction of the pillars at the maximum possible deformation of the triple line when it recedes on the textured surface, θ_{r1} (θ_{r2}) the receding contact angle on the more wetting surface (less wetting surface which is interconnected).

$$f_{eff} = \frac{\cos \theta_r - \cos \theta_{r2}}{\cos \theta_{r1} - \cos \theta_{r2}} \tag{C.2}$$

For super-hydrophobic surface, one can suppose θ_{r2} to be equal to 180°, then



Figure C.8: Effective fraction of the pillar in receding contact angle in function of the maximum pillar fraction of a non-distorted TCL compared to Raj et al model (black solid line). The purple dotted line is the estimated prediction of the data collected from references [23], [69], [70], [77].

Figure C.8 shows the evolution of the effective pillar fraction in function of the maximum pillar fraction of a non-distorted triple line. The effect of the pillar size per unit length of the TCL is correctly predicted by the Raj and al model. However, contrary to this model, it seems that from experimental data for $f_{eff} = 0$ ($\theta_r = \theta_{rair} = 180$) the corresponding pillar fraction is not null, supposing that the possibility to have super hydrophobic surface with contact angle near to 180°. In fact some experiments have demonstrated this possibility with micro/nano-structured water-repellent surfaces [23], [64], [77], [131], [132].

In their model Reyssat and Quéré [63] proposed a simple model with diluted defects (pillar) to predict contact angle hysteresis on textured surfaces. Figure C.9 shows a good agreement with the collected experimental data.



Figure C.9: Contact angle hysteresis in function of solid fraction. Comparison between the prediction of Raj et al model [65] (blue solid line), Reyssat and Quéré model with a_{rq} [63] (black solid line) to some experimental data from references[23], [69], [70], [77].

Raj et al model predicts larger hysteresis in comparison to the experimental data at low Cassie fractions ($f_s < 0.4$), but there is a good agreement at high solid fractions (($f_s > 0.4$)). However, Reyssat and Quéré model predict more precisely contact angle hysteresis at low Cassie fraction but not at high Cassie fraction. In fact, Reyssat and Quéré incorporated in their model a fitting parameter (a_{rq}) to capture the details of the contact line with an assumption that the pillars are dilute such that each defect independently distorts the contact line. Thus, the model was specified to be valid only up to a certain critical solid density of 40%, which is in the same order than the collected data in this work (Figure C.9). At high Cassie fraction, Raj and al model which is a thermodynamic approach including the effect of the contact line distortion seems to be more relevant.

In this part, we have compared contact angle hysteresis of the collected data from literature. These experimental data for hydrophobic surface show that when the drop is in composite state (or fakir or Cassie state) then the advancing contact angles are nearly constant, due to the interconnectivity of the less wetting defect (air) that the drop will follow when advancing.

The so called "Cassie on line" relations with the local line fraction factors along TCL which have successfully predicted some experimental data[21], [62], [65], [74], [130] have been applied and compared to the collected data. We conclude that the model of Reyssat and Quéré [63] and based on the approach of Joanny and de Gennes [62] well predicts the contact angle hysteresis for low solid fraction (dilute defects) surfaces. But global thermodynamic approaches seem to be more relevant for surfaces with high solid fraction.

C.4.Heterogeneous surfaces

As in homogeneous textured surfaces, "Cassie on line" models can be applied to chemically patterned surfaces to predict contact angle hysteresis. Assuming that the contact angle hysteresis depends on how the triple contact line is pinned and deformed on patterned surfaces, one can calculate the effective fraction of the patterns corresponding to the measured contact angles.

$$f_{eff,rec} = \frac{\cos \theta_r - \cos \theta_{r2}}{\cos \theta_{r1} - \cos \theta_{r2}}, f_{eff,adv}$$

$$= \frac{\cos \theta_r - \cos \theta_{r2}}{\cos \theta_{r1} - \cos \theta_{r2}}$$
(C.4)

With '1' indicating the patterns and '2' the substrate.

The evolution of the effective area fraction in Figure C.10 is in good agreement with the model [63], [65]. The effective area fraction varies linearly with the linear fraction of the patterns.



Figure C.9: Effective fraction of the pattern in receding (empty marks) and advancing (full marks) contact angle in function of the maximum pattern linear fraction of a non-distorted TCL. Data collected from references [84] *(in blue),* [15] *(in red) and* [65] *(in purple).*

D Maximum spreading diameter

The maximum spreading diameter can be calculated from an energy balance between the initial time (t=0) of the spreading with diameter D_0 and velocity U_0 and the instant $t = \tau^*$ of the order $\frac{D_0}{U_0}$ where the drop reaches it maximum diameter D_{max} at zero speed (U = 0).

$$\frac{1}{2}\rho U_0^2 \left(\frac{\pi}{6}D_0^3\right) + \pi D_0^2 \gamma_{LV} = E_{s_{max}} + E_{diss}$$
(D.1)

Where $E_{s_{max}}$ is the surface energy at the maximum spreading and E_{diss} the energy dissipated during the spreading.

The major part of the energy dissipation occurs in the corners of the drop near the triple line (0.1 mm from the corners of the triple line), dissipation in the bulk is negligible.

de Gennes [133] demonstrated that the dissipated energy E_{diss} depends on the dynamic viscosity of the fluid η , the triple line velocity $U = \frac{dR}{dt}$ and the instantaneous contact angle θ .

$$E_{diss} = c \frac{\eta}{tan\theta} U^2 \tag{D.2}$$

The constant c is in the order of 30.

For highly viscous liquids, where the kinetic energy is completely dissipated by viscous effects, i.e. $We \gg \sqrt{R_e}$, or $P = \frac{We}{R_e^{4/5}} > 1$.

Chandra et al. [134] and Pasandideh-Fard et al. [103] proposed another relation for the viscous dissipation:

$$E_{diss} = \frac{\pi}{3} \rho U_0^2 D_0 D_{max}^2 \frac{1}{\sqrt{R_e}}$$
(D.3)

To calculate the surface energy $E_{s_{max}}$ a model for a drop shape is needed. At the maximum spreading, the drop looks like a puddle of diameter superior to the capillarity length κ^{-1} [135]. The drop thickness can be given by:

$$h_d = 2\kappa^{-1} \sin\left(\frac{\theta_Y}{2}\right) \tag{D.4}$$

Considering the drop accelerating $a_g = \frac{U_0^2}{D_0}$ instead of gravity g, the drop thickness writes:

$$h_d = \sqrt{2} \left(\frac{\gamma D_0}{\rho V_0^2} (1 - \cos \theta_Y) \right)^{1/2} \tag{D.5}$$

The surface energy $E_{s_{max}}$ at the maximum spreading diameter is then given by [104]:

$$E_{s_{max}} = \frac{\pi}{4} D_{max}^2 \gamma_{LV} (1 - \cos\theta_Y) + \pi D_{max} h_d \gamma_{LV}$$
(D.6)

Taking into account the previous relationships, the maximum spreading diameter is given by the relation [103], [104]:

$$(We + 12)\frac{D_{max}}{D_0} = 8 + \left(\frac{D_{max}}{D_0}\right)^3 \left(3(1 - \cos\theta_Y) + 4\frac{We}{\sqrt{R_e}}\right)$$
(D.7)

If the part of the surface energy from the drop thickness h_d is negligible, then the maximum spreading diameter reduces:

$$\frac{D_{max}}{D_0} = \sqrt{\frac{We + 12}{3(1 - \cos\theta_Y) + 4\left(\frac{We}{\sqrt{R_e}}\right)}}$$
(D.8)

For highly viscous liquids ($We \gg \sqrt{R_e}$), the last equation results in the following relationship:

$$\frac{D_{max}}{D_0} \approx Re^{1/4} \tag{D.9}$$

Another formulation of viscous dissipation has been proposed by Clanet et al [105] which has been validated for silicone oils and aqueous solutions of glycerol. This formulation leads to the same relation that Eq. D.8 with different power law in 1/5.

In the case of inviscid liquid ($We \ll \sqrt{R_e}$), Eq. D.7 leads to:

$$\frac{D_{max}}{D_0} \approx W e^{1/2} \tag{D.10}$$

However, experiments for low viscosity liquids [105] led to different power law. Indeed, the kinetic energy is not completely dissipated by viscous effects, the effects of inertia energy must be taken into considerations. Thus, using the mass conservation between the initial time (t=0 second) and the instant $t = \tau^*$ the drop reaches it maximum diameter, Clanet et al [105] proposed:

$$\frac{D_{max}}{D_0} = \sqrt{\frac{2}{3 h_d} D_0} \tag{D.11}$$

Then

$$\frac{D_{max}}{D_0} \approx c \left(\frac{We}{1 - \cos \theta_Y}\right)^{1/4} \tag{D.12}$$



ÉCOLE DOCTORALE Sciences mécaniques et énergétiques, matériaux et géosciences (SMEMAG)

Titre : Mouillage des surfaces hétérogènes texturées fer-silice par le plomb liquide.

Mots clés : chute de goutte, surfaces texturées, métal liquide, dynamique de mouillage.

Résumé : Dans la galvanisation à chaud, les aciers sont protégés contre la corrosion par une mince couche de zinc obtenue par immersion dans un bain d'alliage de zinc. Avant ce processus, les tôles d'acier subissent un recuit de recristallisation afin d'éliminer l'écrouissage après laminage à froid. Les conditions de recuit utilisées réduisent le film d'oxyde de fer natif, ce qui favorise la mouillabilité de la surface de l'acier par le zinc liquide. Cependant, les nouveaux aciers à haute résistance contiennent des quantités importantes d'éléments d'addition, tels que le silicium et le manganèse. Ces élements diffusent à la surface de l'acier pendant le recuit de recristallisation et forment des particules ou des films d'oxyde par oxydation sélective externe. Si le fer pur est bien mouillé par le zinc liquide, ces oxydes ne le sont pas et leur présence à la surface peut entraîner des défauts dans le revêtement final.

Pour étudier l'influence de la taille et de la distribution des oxydes sur le mouillage par le métal liquide, nous avons étudié un mouillage non réactif du plomb liquide sur une surface hétérogène texturée Fe / silice en utilisant la technique de chute de goutte.

Ces surfaces ont été conçues par dépôt chimique en phase vapeur assisté par plasma, suivi d'un procédé photolithographique.

Après l'impact, la goutte s'étend jusqu'à son diamètre d'étalement maximal. S'ensuit une phase de recule de la goutte. Pendant son recul, la goutte est plus ou moins retenue, en fonction du taux de couverture de silice, sur le fer pur: phénomène d'accrochage-glissement. Sur les surfaces à faible teneur en silice, ce phénomène entraîne une déformation de la forme de la goutte qui est plus allongée dans un sens et quelquefois à la division de la goutte.

Il a été démontré que le mouillage est affecté principalement par la fraction de surface de la silice.

Enfin, nous avons modélisé les différentes phases de l'étalement de la goutte sur ces surfaces hétérogènes. Des modèles de littérature ont été revus et adaptés et nous avons proposé des modèles macroscopiques de l'oscillation de la goutte pendant son étalement.



ÉCOLE DOCTORALE Sciences mécaniques et énergétiques, matériaux et géosciences (SMEMAG)

Title: Wetting on heterogeneous metal-oxides regular patterned surfaces by a non-reactive liquid metal (lead).

Keywords: drop impact, tailored surfaces, liquid metal, wetting dynamics.

Abstract: In hot-dip galvanizing, steel sheets are protected against corrosion by a thin layer of zinc obtained by immersion in a zinc alloy bath. Before this process, the steel sheets undergo recrystallization annealing to eliminate stresses after cold-rolling. The annealing conditions used reduce the native iron oxide film, which promotes the wettability of the steel surface with liquid zinc. However, new high-strength steels contain significant quantities of addition elements, such as silicon and manganese. These elements diffuse on the surface of the steel sheets during recrystallization annealing and form oxide particles or films by selective external oxidation. If pure iron is well wet with liquid zinc, these oxides are not and their presence on the surface can lead to defects in the final coating.

To study the influence of oxide size and their distribution on liquid metal wetting, we studied a non-reactive wetting of liquid lead on a heterogeneous Fe / silica textured surface using the dispensed technique.

These surfaces were designed by plasmaassisted chemical vapour deposition followed by a photolithographic process.

After impact, the drop extends to its maximum spreading diameter. This is followed by a phase of drop receding. During this, the drop is more or less retained, depending on the silica coverage rate, on the pure iron: stick-slip motion. On surfaces with low silica content, this phenomenon causes a deformation of the drop shape which is more elongated in one direction and sometimes at the division of the drop.

We showed that wetting is mainly affected by the surface fraction of silica.

Finally, we modelled the different phases of drop spreading on these heterogeneous surfaces. Literature models were reviewed and adapted and macroscopic models of the oscillation of the drop during its spreading were proposed.