In Chapter 2 and particularly in section 2.3.1 we mentioned that during the spreading of a liquid over a non-ideal solid substrate, the contact line can stay pinned at sharp edges until the contact angle exceeds a critical value, which differs from the Young’s angle. At equilibrium, this is known as the Gibbs’ criterion.

In this chapter, we show experimentally that for the completely wetting volatile liquids used so far there also exists a dynamically-produced contribution to the critical angle for depinning, which could be linked to the evaporation-induced contact angle. The experimental results are also compared qualitatively with the predictions of a thin-film model (inspired by Morris [2001], Rednikov et al. [2009], Todorova et al. [2012]), which we use here for the study of drop depinning formulated in 2D geometry. The simulations have indeed confirmed our experimental observations, namely that there exists a dynamically produced critical angle for depinning, which increases with the evaporation rate. This suggests that one may introduce a simple modification of the Gibbs’ criterion for (de)pinning, that accounts for the non-equilibrium effect of evaporation (Tsoumpas et al. [2014]).

Nevertheless, our study is not restricted only to these observations but it also reaches to the possible effect of the contact line velocity on the depinning angle.

### 6.1 Gibbs’ Criterion

Geometrical features on the surface of a rigid substrate, such as small-scale steps, grooves or other defects, pose an energy barrier hindering the motion of droplets or liquid films. The current understanding of this contact line pinning/depinning phenomenon is based on the Gibbs’ criterion (Gibbs [1906]), which is graphically illustrated in Fig. 6.1 in the case of a single sharp edge on an otherwise smooth substrate. In particular, depinning of a contact line from the edge is deemed to occur when its apparent contact angle with respect to the horizontal exceeds the critical value.
\[ \theta_{cr} = \theta + \alpha \]  

where \( \alpha > 0 \) is the angle between the horizontal and the solid surface after the edge, and \( \theta \) is generally taken as the Young’s angle characterizing the given liquid/solid interface.

A study by Oliver et al. [1977] has confirmed the validity of the above criterion for various liquids by performing experiments on edges subtending a range of angles. Another contemporary work (Bayramli and Mason [1978]) particularly focused on the case of perfectly wetting liquids for which one might intuitively think that such a liquid would never get pinned and consequently that Eq. (6.1) would not be valid. Nevertheless, the experimental results confirmed the Gibbs’ criterion even in the case of complete wetting.

Studies have also been performed to determine the critical height of a surface discontinuity necessary to pin an advancing contact line with the reported values being of the order of a few nanometers (Mori et al. [1982], Ondarçuhu and Piednoir [2005]).

Here, we concentrate on our attention to the effect of evaporation on the depinning contact angle and particularly on whether Eq. (6.1) more generally holds out of equilibrium, i.e., when the contact angle \( \theta \) is influenced (or even entirely determined) by hydrodynamics and heat mass transfer.

This phenomenon can possibly be of relevance to several applications of which contact line (de)pinning is a crucial process; a few examples include microfluidics (Herminghaus et al. [2008]), condensation on structured substrates (Enright et al. [2012]), dewetting (Ondarçuhu and Piednoir [2005]) and nanowire growth (Schwarz and Tersoff [2009]).

### 6.2 Experimental Methods

#### 6.2.1 Groove Fabrication

For the purposes of our experiments, we have fabricated a microscopic groove on a defined region of a 3\( \text{mm} \) thick polycarbonate plate. The groove delimits a circular region with a radius of 5\( \text{mm} \).
6.2. EXPERIMENTAL METHODS

Figure 6.2: The excimer laser has the ability to break the chemical bonds in a polymer, while a mask allows us to control the area of the material that burns out. From Crafer and Oakley [1992].

Microgrooves can be fabricated using techniques such as lithography (Xia and Whitesides [1998]), micro-milling (Bang et al. [2005]) or excimer laser (Crafer and Oakley [1992]), the latter method being the one we apply here. Generally speaking, an excimer laser can produce light of high energy and, along with a high precision, it ensures high efficiency making it a valuable tool concerning material removal applications. The main difference of this type of laser in comparison with other laser techniques lies in the energy of the beam which turns the exposed material from solid directly to vapor by breaking the molecules apart into individual atoms.

To define the area that should be exposed to the excimer laser, a mask comes between the substrate and the source of the laser beam (Fig. 6.2). In our case, a square mask is used. The shape of the mask actually determines the shape of the groove profile which is measured here using a 3D laser scanning confocal microscope (Keyence VK-X200). The acquired images indicate that the profile, and consequently the geometrical angle $\alpha$, varies gradually along the groove. This is because the mask retains its orientation as it follows its circular path (Fig. 6.3a), therefore cross sections of different shapes are produced (Fig. 6.3b-e).

Yet, from Eq. (6.1) it follows that the only parameter that determines the depinning angle $\theta_{cr}$ is the slope of the groove. Therefore, the depinning of the contact line should occur at the cross sections with the smallest possible slope. In particular, these are found to lie at the four locations where the groove adopts a V-shape profile, i.e., where the trajectory of the mask is aligned to its diagonal. This triangular shape is obtained because the number of laser bursts is maximum along the diagonal of the mask and it decreases, tending to zero, away from it (Fig. 6.3a). Hence, the excimer laser burns away more material from the center of the groove than from the edges.

After scanning the groove with the 3D digital microscope, we obtain approximately 14000 profiles that correspond to the parts of the groove with a triangular-like cross-section. We then calculate the geometrical angle $\alpha$ of each one of them. The minimum value is found to be $\alpha = 36.6 \pm 1^\circ$.

6.2.2 Experimental Apparatus and Procedure

Placing the sample in a tensiometer (Kruss FM40 EasyDrop) enables one to follow the drop from its creation till depinning and to measure its apparent macroscopic contact angle with respect to the horizontal. In the present study we focus on the critical angle $\theta_{cr}$ at which the depinning occurs.

A 500$\mu$l syringe (with an internal diameter of $\sim 0.5\text{mm}$) is mounted on the dosing system, manipu-
CHAPTER 6. EFFECT OF EVAPORATION ON CONTACT LINE DEPINNING

Figure 6.3: (a) Several positions of the mask with respect to its circular path; (b) when the trajectory of the mask is aligned with its diagonal a V-shaped cross section is generated whereas (c) a U-shaped profile is observed when the trajectory is aligned to the sides of the mask; (d,e) 3D images of the parts of the groove corresponding to triangular and rectangular profiles, respectively, taken with a laser confocal microscope.

lated by an accompanying relevant software, while the sample is placed on a stage below it (Fig. 6.4). During the tests, the liquid is continuously being injected on the substrate in the region surrounded by the groove. The backlight technique and a fixed CCD camera are used to visualize and record the evolution of the drop, respectively. The experiments are taking place inside a clean room, therefore constant environmental conditions are well ensured. Moreover, the whole tensiometer is covered by a nylon encasement to prevent the strong air circulation present in the room from affecting the evaporation rate.

A typical experiment is depicted in Fig. 6.5. At a first stage, the liquid has just been deposited on the substrate (Fig. 6.5a), and with further liquid injection the droplet grows and gets flattened by gravity. At some moment, the contact line is pinned at the inner edge of the groove (Fig. 6.5b), and remains so while its contact angle increases until it reaches the critical angle for depinning (Fig.6.5c). This moment is easily detected as the “puddle” then rapidly floods the rest of the substrate (Fig. 6.5d). Note that only half of the drop is present in the field of view of the camera in order to achieve the largest possible magnification. Moreover, to avoid having the syringe in the field of view we place it closer to the opposite edge from the one on which we focus. Thus, the injected liquid advances in a non-axisymmetric way.

With the tensiometer we measure the apparent contact angle and the height of the drop at the moment of depinning as well as the total experimental time, i.e., the time elapsed between the moment that the very first drop exits the needle of the syringe till the moment of depinning. Having the total time and multiplying it by the injection rate we can calculate the total injected volume.

Ten independent experiments are performed for HFE-7100, 7200 and 7500 and for eleven different injection rates, i.e., for 50, 75, 100, 150, 200, 250, 500, 750, 1000, 1250 and 1499.7 µl/min, with the latter being the maximum reachable one. The minimum injection rate corresponds approximately to the rate at which a drop of HFE-7100 (or 7200) can slowly reach the groove and grow up until it breaks. For lower values, the evaporation rate exceeds the injection speed and no pinned drop of HFE-7100 can be formed. The equivalent injection rate for HFE-7500 is about 5 µl/min. Experiments at this rate are also performed for this particular liquid.
6.2. EXPERIMENTAL METHODS

- Light Source
- CCD Camera
- Liquid Deposition System
- Stage

Figure 6.4: FM40 EasyDrop Tensiometer and its working principle.

Figure 6.5: Experimentally-obtained side views showing a part of a quasi-steadily evaporating droplet at different stages together with schematic representations (insets): (a) free, (b,c) pinned at the groove edge, and (d) depinned contact line.
CHAPTER 6. EFFECT OF EVAPORATION ON CONTACT LINE DEPINNING

As the images of Fig. 6.5 indicated, we are observing just one side of the groove. Before each test starts, the sample is placed on the tensiometer with a different orientation to check other sides of the groove as well. The cleaning procedure is similar to the one mentioned in the previous chapters. Moreover, in order to exclude the possibility that the substrate and particularly the groove keeps any memory of the previous experiment, which would make our results biased, we perform the tests in a random order as far as the injection speed and the liquid is concerned. Nevertheless, during the experiments the drop is sensitive to vibrations and apparently the larger the drop the more sensitive it is. Thus, it is rather likely that the drop will depin easier from the groove in case of an abrupt movement. Hence, although an extreme care was taken not to disturb the tests, it is still possible that slight vibrations could have occurred introducing some uncertainty in the obtained results. Another main source of uncertainty is any possible tilt of the substrate which would result in an uneven distribution of the contact angle and therefore in a faster depinning of the drop. Thus, before conducting the experiments we make sure that the stage of the tensiometer and consequently the groove are placed as horizontal as possible, eliminating the effect that a tilted surface would have on our tests. In the end, a rather satisfactory reproducibility is achieved.

6.3 Results

The results are shown in Fig. 6.6. The error bars indicate twice the standard deviation resulting from averaging the critical values of the ten experiments conducted for each case. Specifically, in Fig. 6.6a one can read the critical angle for each liquid and the injection rate. Initially, we focus only on the smallest possible injection rate. We see that the critical angle is not only larger than the geometrical angle of the groove (36.6±1°) but does also depend on the liquid. Namely, the depinning angle is 38.4±1.8° for HFE-7500 (at 5μl/min), 42.2±2.5° for HFE-7200 (at 50μl/min) and 44.8±1.5° for HFE-7100 (at 50μl/min). The apex of the drop at that moment is measured at 0.75±0.04mm for HFE-7500, 0.81±0.02mm for HFE-7200 and 0.83±0.04mm for HFE-7100 (Fig. 6.6b). These results indicate that when strongly volatile liquids are considered the depinning occurs for slightly larger droplets.

If we now turn our attention to the full range of injection rates, we see that this parameter, too, affects the depinning angle, specifically regarding HFE-7500. In particular, we see that as the injection rate increases the depinning angle for the three liquids converges to the corresponding value of HFE-7100. Similar observations, yet less pronounced, can be made by looking Fig. 6.6b.

As far as the experimental time is concerned (Fig. 6.6c), this varies strongly depending on the injection rate and the liquid. For instance, by increasing the injection rate the breaking of the drop occurs faster. Apparently, this is because we reach the critical angle much earlier. Evaporation plays an important role in this respect, as well. For low injection rates evaporation delays the growing of the droplet, while for higher injection speeds the depinning happens so fast that there are practically no evaporation losses; hence the total experimental time becomes approximately the same for all the liquids. Indicatively, for HFE-7100, HFE-7200 and HFE-7500 and 50μl/min the total experimental time is 105s, 70s and 50s, respectively. For HFE-7500 and 5μl/min the experimental time is approximately 10 minutes. Nevertheless, for injection rates larger than 500μl/min the experimental time converges for the three liquids reaching the value of 1.5s for the fastest injection rate. By plotting the results in a log-log scale (Fig. 6.6d) we notice that the experimental time for HFE-7500 follows a power law. Indeed, the experimental points (excluding the first one for which evaporation has a significant effect on the experimental time) can nicely be fitted by the following function (Fig. 6.6e)
6.4 Discussion

6.4.1 Comparison with the Classical-Static Shape Theory

In order to verify that the above results are meaningful we compare them with the predictions of the classical static shape theory (excluding any Marangoni contributions). As the contact angles considered here are rather large we cannot use the linearized approach of section 5.2.1; therefore we solve the full non-linear second-order differential equation that describes the static shape of the drop numerically (using Mathematica). If \( r = 0 \) corresponds to the center of the drop of a radius of approximately 0.5 cm, then the applied boundary conditions ensure that the contact line is pinned at the edges, i.e., \( h(0.4745) = 0 \), and that the slope at the apex of the drop is zero, i.e., \( h'(0) = 0 \).

By matching the contact angles extracted from the experiment and the model, we compare the corresponding heights and volumes. The comparison, shown in Fig. 6.7, indicates that the experimental results, namely the obtained \{angle, height, volume\} triads, are indeed realistic. The difference between the injected volume and the volume predicted by the model as far as slow injection rates are concerned is expected and attributed to the volume lost due to evaporation. For less volatile liquids this divergence becomes less apparent even for slow injections. In fact, for more accurate results the model should be compared with the droplet volume just before depinning, and not with the total injected volume. The agreement for the height is more telling in this regard.

6.4.2 Evaporation-Influenced Gibbs’ Criterion

Now to explore whether the difference between the measured critical angles and the theoretical ones, suggested by the classical Gibbs’ criterion, is linked to evaporation, we calculate from Eq. (6.1) the value of \( \theta \), using the measured values \( \theta_{cr} \) and \( \alpha \), and we compare it to the corresponding apparent contact angle induced by evaporation, given in Chapter 4 and denoted here by \( \theta_{ev}^{app} \). Although the present configuration is different from the one described previously in Chapter 4 (e.g. receding instead of advancing contact line), the corresponding evaporation-induced contact angles are here assumed not to differ significantly.

\[
t = 42.62q^{-1.015}
\]

where \( t \) is the experimental time in sec and \( q \) is the injection rate in \( \mu l/sec \). Since the power in Eq. (6.2) is really close to -1, the coefficient 42.62 should approximately describe the volume of the drop (in \( \mu l \)) that should lead to the depinning of the contact line for the specified range of injection rates. Indeed, by calculating the overall injected volume for HFE-7500 (Fig. 6.6f) we do find an almost constant value, i.e., 39 \( \mu l \), independent of the injection rate, which is close to the aforementioned value. The difference between the two values is due to the fact that in Eq. (6.2) the experimental time is not exactly inversely proportional to the injection rate. Of course, for 5 \( \mu l/min \) the calculated injected volume is significantly larger since a portion of it is lost due to evaporation. Similarly, for HFE-7100 and 7200, we retrieve the same constant value, for the overall injected volume, as above but only for the injection rates larger than 500 \( \mu l/min \) for which evaporation can be considered negligible.

*The actual radius of the drop is taken slightly smaller than 0.5 cm, since we exclude an average value of the width of the groove
Figure 6.6: (a) Apparent contact angle and (b) apex of the drop at the moment of depinning as well as (c) total experimental time in linear and (d) logarithmic scale for various HFEs; (e) total experimental time only for HFE-7500; (f) calculated total injected volume for various HFEs. All values are plotted versus the injection rate.
6.4. DISCUSSION

Figure 6.7: Assuming the same apparent contact angle we plot together the results of the static model and the experiments for the apex and volume: (a,b) HFE-7100, (c,d) HFE-7200 and (e,f) HFE-7500.
To assume a quasi-steady regime and to rule out any effect of contact line speed, while the drop is advancing towards the groove, we perform this comparison only for the smallest possible injection rate for each liquid, for which the capillary number is sufficiently small. The results, shown in Table 6.1, indicate indeed a very satisfactory agreement suggesting that one may introduce a simple modification of the Gibbs’ criterion as follows

$$\theta_{cr} = \theta_{ap}^{ev} + \alpha \quad (6.3)$$

where, as compared to Eq. (6.1), it is the evaporation-induced angle that takes the place of the Young’s one.

In principle, one could try to explain the difference in the critical angle that occurs among the three different liquids on another basis, which would eventually rule out the hypothesis of a modified Gibbs’ criterion. Specifically, one could argue that, in the course of an experiment, liquid is slowly invading the groove which is eventually filled completely causing inevitably the depinning. This must be deemed less likely for HFE-7100 or 7200 simply because these are more volatile than HFE-7500 and the amount of liquid that enters the groove will evaporate allowing the drop to reach larger angles. An extra factor that can be used to support the above argument is that the depinning angle for HFE-7500 increases with the injection rate. In line with what was just mentioned, this could be exactly because of the time the liquid needs to fill in the groove and this time is ensured only when injection is slow. For fast injections there is time for the pinned drop to reach the critical angles before breaking. Although these assumptions could hypothetically explain the difference (similarity) between the critical angles for the three liquids and for slow (fast) injection rates, they still do not provide a satisfactorily defined critical angle for depinning that would also be in accordance with the classical Gibbs’ criterion.

Yet, in an attempt to verify whether the liquid is invading the groove long before the depinning takes place, we perform a 40 minute experiment with HFE-7500. The injection rate is really low and constantly regulated between 2 and 5 µl/min so that the contact angle is maintained close to (but lower than) the critical angle. If there were any kind of continuous leak then the breaking would apparently occur at the very beginning of this sufficiently long experiment. Nevertheless, the depinning occurred at an angle slightly larger than 36°.

In addition to this test, we also conduct top-view experiments by placing the grooved substrate in the Mach-Zehnder interferometer. The injection rate is not controlled as in the previous experiments but is kept at very low levels. Since the the drop is too large we cannot follow its apparent angle but we can determine whether and when the liquid enters the groove with respect to the moment of depinning. These qualitative experiments showed that the liquid indeed leaks into the groove but just slightly before depinning, i.e., approximately 0.10s earlier. Nevertheless, we do know from the tensiometer experiments that 0.10s is not enough to increase the pinned angle when the injection rate is lower than 750µl/min. For faster injections the pinned angle can be increased by at most 2° in 0.10s.

Table 6.1: Experimentally determined critical angle at depinning $\theta_{cr}$ (measured by tensiometry); its difference with the geometrical groove angle $\alpha$ is compared to the experimentally determined evaporation-induced apparent contact angle $\theta_{ap}^{ev}$ (measured by interferometry in the setup discussed in Chapter 3).

<table>
<thead>
<tr>
<th>Liquid</th>
<th>$\theta_{cr},^{\circ}$</th>
<th>$\theta_{cr} - \alpha,^{\circ}$</th>
<th>$\theta_{ap}^{ev},^{\circ}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HFE-7100</td>
<td>44.8±1.5</td>
<td>8.2±2.5</td>
<td>8.8±1.0</td>
</tr>
<tr>
<td>HFE-7200</td>
<td>42.2±2.5</td>
<td>5.6±3.5</td>
<td>6.0±1.0</td>
</tr>
<tr>
<td>HFE-7500</td>
<td>38.4±1.8</td>
<td>1.8±2.8</td>
<td>3.4±0.5</td>
</tr>
</tbody>
</table>
Overall, we can reasonably conclude that the observed leak accompanies indeed the depinning process but it is not the one that causes it.

6.4.2.1 Theoretical Approach†

This experiment-based conjecture is now examined on the basis of a thin-film model valid for the case of a highly wetting liquid on a smooth superheated substrate. Given that the corresponding theory for diffusion-limited evaporation into air generally involves non-local operators (Eggers and Pismen [2010]), we here consider the mathematically simplest problem of a droplet evaporating into its own vapor. Below we describe shortly the key points of the developed theory followed by some of the main results, whereas for more details one could consult the study of Rednikov et al. [2009] and Todorova et al. [2012].

In particular, we study the case of a two-dimensional sessile drop of a perfectly wetting liquid fed by an influx $S(x)$ on a topographically structured substrate $\eta(x)$. Solving the problem in the lubrication approximation, with a stress-free interface and a no-slip bottom, one can derive the following dimensionless evolution equation for the film thickness $h(x)$ (see Fig. 6.1), which for a steady state (assuming that the influx compensates integrally for the evaporation flux) reads

$$-\frac{\partial q}{\partial x} - Ej + S = 0$$  \hspace{1cm} (6.4)

where $q(x)$ is the horizontal volume flux inside the drop and $j$ is the evaporation flux density, given by

$$q = \frac{h^3}{3} \frac{\partial \Omega}{\partial x}, \quad j = 1 - \frac{\Omega}{K + h}, \quad \Omega = \frac{1}{h^3} + 3 \left(\frac{\partial^2}{\partial x^2}(h + \eta) = h^{-3} + 3(h'' + \kappa)\right)$$  \hspace{1cm} (6.5)

†The theoretical work has been realized in collaboration with Dr. Mariano Galvagno and Professor Uwe Thiele.
CHAPTER 6. EFFECT OF EVAPORATION ON CONTACT LINE DEPINNING

with $\Omega$ being the pressure variation in the liquid including both the capillary and the disjoining pressure components. The latter considers only the long-range Van der Waals interactions to model a complete wetting situation. In the above equations, $E$ and $K$ are the evaporation number, which shows how strong the effect of evaporation is (weak for $E \ll 1$), and the kinetic resistance to evaporation, respectively. The scales are chosen so that the disjoining pressure and the capillary pressure contributions are of the same order of magnitude.

To model the inner edge of our groove, we consider a slope kink $\eta'(x) = -\alpha [1 + \tanh((x-c)/w)]/2$, separating a horizontal region ($x \ll c$) from a region with downward slope $\alpha$ (for $x \gg c$). Hence, the curvature is given by $\kappa(x) = -\alpha \text{sech}^2((x-c)/w)/2w$, i.e., peaking in a region of width $w$ around the bend at $x = c$ (the larger the length scale $w$ the smoother the curvature of the substrate at the bend). Boundary conditions are $h'(0) = h'''(0) = 0$ (symmetry at $x = 0$), while at $x = L \gg c$, we impose a flat equilibrium microfilm, i.e., $h(L) = 1$ and $h'(L) = 0$. This 4-th order problem is solved with the help of the auto07p continuation package (Doedel et al. [1991], Dijkstra et al. [2014]), using typical values $E = 0.124$ and $K = 5.74$ as a reference case (Rednikov et al. [2009]). Selected typical results are presented in Fig. 6.8.

The left plot shows that small droplets indeed display a non-vanishing evaporation-induced angle $\theta_{ap}^e$, despite the perfectly wetting situation (Todorova et al. [2012]). The value of this apparent angle (defined as the slope at $z = 0$ of a parabola fitting the droplet at its apex) is read in Fig. 6.8b for sufficiently negative $x_0 - c$ ($x_0$ is where the parabola intersects $z = 0$). One notes that, $\theta_{ap}^e$ increases with $E$ and decreases with $K$, as parametrically studied by Rednikov et al. [2009]. When increasing the influx, the droplet increases in size (Fig. 6.8a) and eventually reaches the edge where the contact line remains pinned, while the apparent angle increases (Fig. 6.8b). At larger influxes, the droplet eventually depins and spreads on the sloped part of the substrate (Fig. 6.8a), with an apparent contact angle now close to $\theta_{ap}^e + \alpha$ (Fig. 6.8b for positive $x_0 - c$). This apparently holds whatever are the values of $E$, $K$, and $\alpha$, which numerically validates our improved Gibbs’ criterion. Note that our theory predicts a continuous transition of the apparent contact angle between its extreme values $\theta_{ap}^e$ and $\theta_{ap}^e + \alpha$ when the contact line crosses the edge. This mesoscopic effect is also predicted by equilibrium density-functional theory (Dutka et al. [2012]), due to the existence of the ultra-thin liquid film fully covering the substrate. In general, the fact that the corner is smooth rather than sharp also contributes to rendering the transition continuous. Here, it appears that the width of this “pinning” region is rather determined by the size of the microregion in which the evaporation-induced contact angle is established (i.e., typically the width of the evaporation flux peaks in Fig. 6.8a). These submicrometric length scales become negligible when larger droplets are considered however, such that the transition appears discontinuous in practice (as in Gibbs’ macroscopic picture).

Overall, although the comparison between the experiments and the theory is not exactly one to one, the latter has still allowed to confirm our experimental observations.

6.4.3 Contact-Line-Speed-Influenced Gibbs’ Criterion

We will now investigate whether the injection rate can have any effect on the depinning angle focusing only on the case of HFE-7500 for which an increase of the depinning contact angle with the injection speed is observed (Fig. 6.6a). Moreover, evaporation is the weakest in this case and therefore we can isolate the effect of contact line speed, if any, from the effect of evaporation.

The idea that we are testing here, inspired by Cox-Voinov law, is that as we increase the injection rate the apparent contact angle $\theta_{ap}^{adv}$ with which the drop advances to the groove should also increase. In particular, we examine whether
6.4. DISCUSSION

Figure 6.9: Cubic difference between the advancing apparent contact angle (determined implicitly from the experiment) and the apparent contact angle induced by evaporation versus the injection rate for HFE-7500.

If that would be true we could, hypothetically speaking, substitute $\theta_{\text{adv}}^{\text{ap}}$ in the place of $\theta$ in Eq. (6.1), similarly to what we did in the previous section with the apparent contact angle induced by evaporation. Thus, Eq. (6.6) becomes

$$(\theta_{\text{cr}} - \alpha)^3 - \theta_{\text{ev}}^3 \sim q$$  (6.7)

As $\theta_{\text{ev}}$ we are going to use the the values given in Table 6.1. From the range of injection rates we exclude the first two values for which the left-hand side of the above relation yields a negative value (possibly because in these cases $q$ is comparable with the evaporation rate). The results plotted in Fig. 6.6b show that the term $(\theta_{\text{adv}}^{\text{ap}})^3 - \theta_{\text{ev}}^3$ is increasing proportionally with the injection rate except for the case of 750$\mu$l/min, which fails to follow the linear trend.

In other words, one could possibly relate $\theta$ and consequently the Gibbs’ criterion itself to the advancing contact angle. According to this, the depinning will take place as soon as the drop has reached the advancing angle with respect to the inclined surface.

Of course there remains a question why the same effect is not observed in case of the other two liquids. It could be because evaporation is so intense for HFE-7100 and 7200 that the apparent contact angle induced by evaporation is the only one essential, with velocity contributions being negligible.

6.4.4 Square Groove

Tests have been also performed on a non-axisymmetric groove. These experiments, which in fact preceded the ones described above, were conducted on a 5mm thick plexiglass plate. During the groove fabrication, the laser was following a square-like trajectory delineating this time a 10mm square with rounded corners ($r = 1mm$).

The particular type of substrate, however, was not appropriate for the laser used. As a result, the quality of the groove was rather poor which gradually deteriorated and became unable to pin the drop effectively; this is also the reason why we switched to polycarbonate afterwards. Nevertheless, we
Figure 6.10: The profile of a pinned droplet when this is seen from two different perspectives: (a) along one of the sides and (b) perpendicular to the diagonal.

were initially able to conduct a series of experiments for HFE-7100, similar to the one described above.

Although we are still interested in the depinning angle, we first describe a different feature that concerns the distribution of the apparent contact angle around the groove. In particular, we performed 11 experiments per injection rate. During the first 10 experiments we were looking along one side of the groove and actually we focused on its middle point, whereas during the 11th the sample was turned by 45° allowing the camera to record the pinning at the rounded corner; the insets of Fig. 6.10 demonstrate this schematically. Moreover, in the same figure one can see the difference in the way the contact line approaches the groove at these two points. In the middle of a side (Fig. 6.10a) we have a well-defined angle whereas a smoother transition seems to take place at the corner indicating, at first sight, a smaller angle (Fig. 6.10b). The results shown in Fig. 6.11 confirm this observation.

By examining these graphs, we see that the height (Fig. 6.11a), as well as the total experimental time (Fig. 6.11b), concerning the 11th experiment (observing the corner) does not deviate a lot from the results of the previous 10 experiments (observing the edge). Apparently, the same holds for the total injected volume (Fig. 6.11c). This confirms that the 11th test is indeed just a repetition of the same experiment. Thus, one could also expect identical results concerning the apparent contact angle. Yet, this is not the case. In particular, we can see that the critical angles measured by looking at one of the corners of the groove are the same no matter the flow rate but considerably less‡ than the ones measured along the side (Fig. 6.11d). This could be an indication that the apparent contact angle is not uniform along the periphery of the square region but it depends on the point.

In an attempt to substantiate the above conjecture, we once again recur to the classical static shape theory and particularly to Eq. (5.8). With Eq. (5.9), which describes the curvature of the liquid-air interface, and the boundary conditions \( h(x, -1/2) = h(x, 1/2) = 0, h(-1/2, y) = h(1/2, y) = 0 \) (where \(-1/2 \leq x, y \leq 1/2\)), which ensure that the contact line is indeed pinned at the edges, Eq. (5.8) is again solved numerically with the help of Mathematica. The results are again matched for the contact angle measured experimentally at the middle point of the edge and are plotted in Fig. 6.11 along with the experimental ones. According to the theoretical results, the angle at the corner should always be zero.

In Fig. 6.12 we plot a full 3D representation of a pinned sessile square drop of the same base size and apparent contact angle (at the edge) as the drop we obtain experimentally at the moment of depinning. Indeed, as it is more evident in Fig. 6.12 (right), the distribution of the apparent contact angle along a side reaches the maximum in the middle and vanishes as we approach the corner. This can also be seen

‡ We should note here that due to the characteristic shape of the corner profile and the small slope that occurs there, the corner measurements, as far as the angle is concerned, could be far from the true value.
Figure 6.11: Experiments performed for different flow rates while we are focused on the middle point of an edge are compared to experiments during which we are looking at a single corner. The comparison takes place in terms of (a) the apex of the drop, (b) the total experimental time, (c) the calculated total injected volume and (d) the apparent contact angle at the moment of depinning. The results, which concern only HFE-7100, are also compared to the predictions of the classical static model under the premise of the same apparent contact angle at the middle point of the edge.
CHAPTER 6. EFFECT OF EVAPORATION ON CONTACT LINE DEPINNING

Figure 6.12: A three-dimensional plot of the surface of a pinned square-base drop. The apparent contact angle in the middle point of the edge is chosen similar to the experimental one, i.e., $45^\circ$. The bottom right plot shows the distribution of the apparent contact angle along a side of the drop.

Figure 6.13: (a) Middle and diagonal cross-sections of the droplet as well as (b) the respective zooms near the contact line.
6.4. DISCUSSION

(a) (b)

Figure 6.14: (a) Variation of the local contact angle with the angular coordinate along the perimeter of the groove, for a given maximum contact angle around the perimeter and different corner-rounding ratios $R$; (b) minimum contact angle as a function of the ratio $R$, with the maximum contact angle $\theta_A$ varying from $10^\circ$ to $90^\circ$. From Soltman et al. [2013].

in Fig. 6.13a where the theoretical profiles regarding the two droplet cross-sections are demonstrated, and it can be made even more striking if we particularly focus our attention on the region close to the contact line (Fig. 6.13b). There, it becomes clear that while in the middle point of a side the slope of the profile is finite, at the corner not only it is smaller but it also tends to zero. Although a zero angle at the corner is in contradiction with what we had observed experimentally, with the side-view experimental method that we use here it is almost impossible to reliably determine really low contact angles, i.e., lower than $10^\circ$. Another reason is of course that the model considers sharp corners while in our experiments the corners are rounded.

As for a physical (geometrical) explanation of this zero angle near the corner, we note that this is the only possibility of having a smooth droplet surface. Otherwise, if the corner angle was non-zero, we could expect a non-smooth transition from one face of the droplet to another which would imply an infinite curvature at the corner. In this case, the region near the corner would be characterized by a large over-pressure and, therefore, liquid would flow away from the corner, i.e., a static equilibrium shape would not exist.

Our observations are also in agreement with recently published results (Soltman et al. [2010, 2013]). More specifically, Soltman et al. [2013] performed simulations with a surface energy minimization software (Surface Evolver) for static droplets of different corner-radius-to-side-length ratios $R$. These indicate that the minimum contact angle occurs at the rounded corner (Fig. 6.14). This minimum value, however, depends on both the value of the maximum contact angle $\theta_A$ (located at the middle of a side) and on the ratio $R$, i.e., on the level of corner rounding. Yet, for a perfect square it is always zero. Moreover, according to Fig. 6.14b, for $R = 0.1$ and $\theta_A \simeq 45^\circ$, which is the case that corresponds to our experiments, a corner angle of $15^\circ$ should be expected; approximately $5^\circ$ less than what we have measured.

The aforementioned study actually links these facts to substrate roughness and more generally to applications related with patterning through inkjet printed techniques. In particular, they show experimentally that by increasing surface roughness the minimum angle decreases which allows the printing of sharply defined equilibrium corners.
6.4.5 Concluding Remarks

The current chapter showed that Gibbs’ criterion and especially Eq. (6.1) more generally holds out of thermodynamic equilibrium. In particular, evaporation or the speed at which a contact line advances to a defect seem to affect the depinning moment from it, when perfectly wetting liquids are considered. Apart from any fundamental interest that might arise from this result, this alone could possibly lead to advances in various application fields, such as those already mentioned in section 6.1. As a future perspective, one could study partially wetting situations and develop current theories so as to allow a quantitative comparison with the experiments; a first step in theoretical modeling would be, for instance, taking into account a diffusion-limited evaporation into air.

Figure 6.15: Josiah Willard Gibbs (1839-1903); his significant contribution to physical science and mathematics is undisputed. A vast number of his papers can be found in the book "The Scientific Papers of J. Willard Gibbs".