Drop impact on chemically structured arrays

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Abstract
We describe recent investigations on the impact behaviour of liquid drops onto chemically structured surfaces. The surface patterns were prepared via photochemical attachment of polymer molecules with different hydrophilicities using self-assembled monolayers of benzophenone bearing silanes. Immobilization of the polymer monolayers was followed by an ablation process to generate a chemical surface pattern. Impact experiments on systems consisting of very hydrophobic poly(perfluoroalkylethyl)acrylate coatings and hydrophilic areas show that within certain limitations the water drop has a strong tendency to reach the hydrophilic spots, even for inclined substrates. Impact experiments of drops on arrays of hydrophilic spots on the background of a perfluorinated polymer show that the drops spontaneously self-centre on the lithographically generated pattern. The obtained results suggest that the process can be used to circumvent some of the current problems in micro-array fabrication.

1. Introduction

Drop impact phenomena play a significant role in many industrial processes such as fuel injection, spray coating and ink-jet printing. Of particular importance for such processes is the prediction of the final drop position as a function of various parameters such as the drop diameter, the impact velocity and the dynamic viscosity and density [1, 2], especially for high-parallel dispensing systems in combinatorial chemistry applications [3–6]. Moreover, a complex fine-tuning is needed for prefabricated arrays, where in some cases successive printing of different reagents in the very same location is desired. In the majority of cases, the resulting chemical surface modifications are both so thin and small in size, that they can hardly
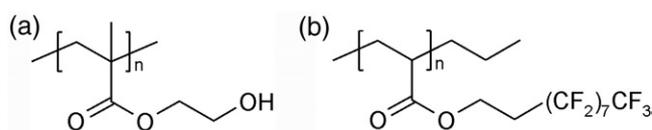
Figure 1. Structures of polymers used for surface functionalization: (a) PHEMA, (b) PFA.

be detected by standard optical methods [7]. This poses a significant problem for finding the same spot again in processes, in which it is desired to print over one spot several times.

Furthermore, the drop ejection process constitutes a further problem in all non-contact printing processes. During printing of liquids with different surface tension, the forces at the rim of the dispensing nozzle vary from liquid to liquid. A specific problem exists if the value of the surface tension of the liquid is relatively low. This may lead to a non-symmetric separation of the drop from the nozzle, so that during the detachment process a force parallel to the surface is exerted on the drop, causing acceleration parallel to the surface. This leads to a deviation of the actual drop position from the desired target zone [8] and/or a strong scattering of the drop positions.

Here, we describe a process in which chemically structured surfaces are used for the control of drop positions in micro-array fabrication. For the preparation of patterned surfaces, a photoactive molecule is immobilized on the substrate in the first step. Second, a thin film of a fluoropolymer is deposited and covalently linked to the surface by UV irradiation. Finally, an ablation step with high energy UV irradiation through a mask leads to controlled decomposition of the polymer in the irradiated areas. During this process the ablated areas become hydrophilic, whereas the polymer coated areas do not become wetted by an aqueous test liquid.

In the following, we show results for single and multiple impact experiments onto chemically structured surfaces. A detailed investigation of the dynamics of the impact process on chemically structured surfaces can be found elsewhere [9].

2. Experimental section

Sample preparation. Surfaces with different hydrophilicities were obtained via a photochemical attachment of poly(hydroxyethylmethacrylate) (PHEMA) and poly(3,3,4,4,5,5,6,6,7,7,8,8, 9,9,10,10,10-heptadecafluorodecylacrylate) [10, 11] (PFA) (figure 1).

First, a self-assembled monolayer of a photoreactive monochlorosilane is covalently linked to a silicon surface (figure 2). Second, a dip-coated layer of homopolymers of defined hydrophobicity is attached by irradiation, yielding polymer layers of several nanometres thickness. This technique can be used for almost any C–H-bond bearing polymer [12].

A subsequent ablation step using a mask leads to a decomposition of the polymer at the irradiated area [13]. The ablation experiments were carried out using a Pen Ray lamp from LOT Oriel, which has a significant output at low wavelength UV light. Typical irradiation times were 12 h. Static contact angles were measured using a Dataphysics OCA20 set-up and Millipore water. The drop size was 2 μl in all cases.

Experimental set-up. The drops are generated using a syringe and needles of 0.9 mm diameter. The drop diameter obviously depends on the needle diameter, and was 2.7 mm for the experiments described here. The drop falls from 20 cm height, which corresponds to an impact velocity of 1.4 m s^{-1}, and passes a light barrier that triggers a CCD camera (Vosskühler HCC 1000 (stroboscope)). A stroboscope with a duration period of 10 μs is used for illumination. Images with a resolution of 1024 $\times$ 512 pixels can be captured with up to 1000 frames s^{-1}.
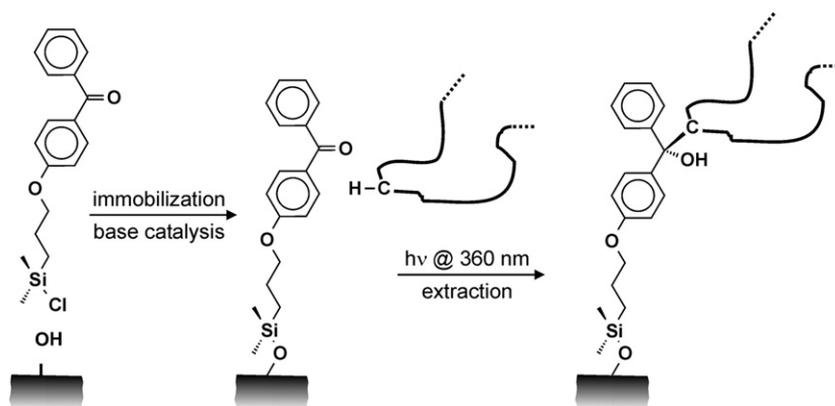
Figure 2. Schematic depiction of the surface functionalization using a photoactive benzophenone group bearing monochlorosilane.
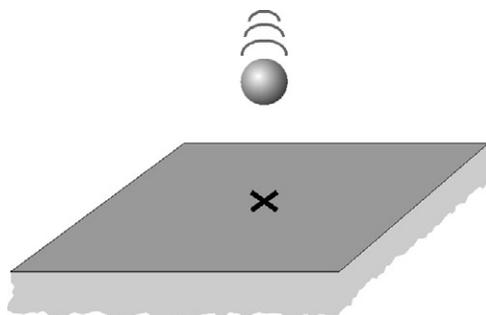

Figure 3. Drop impacting on a homogeneously coated substrate.

For a better visualization of the experiments, in which many drops were printed on the surface of a chemically structured array, a solution of 6 mg (1.8×10^{-5} mol) fluorescein in 20 ml $NaCO_3$ solution (1 wt%) was used. For this set of experiments, we used a needle with a diameter of 0.4 mm, which corresponds to a drop diameter of 2.5 mm. The photographs were recorded using a Canon Power Shot G2 with 4.0 Mega Pixels.

3. Results

For reference experiments, the impact behaviour of water droplets on homogeneously coated PHEMA and poly(perfluoroalkylethyl)acrylate (PFA) surfaces was investigated (figure 3). The two polymers were chosen as models, because the former one is moderately hydrophilic and the latter, like all other fluorinated polymers, strongly hydrophobic. The static contact angle of the PHEMA coating was measured to be $56° \pm 5°$, and the static contact angle measurement of the PFA coating was $110° \pm 4°$.

Figure 4 shows an impact experiment of a water drop onto a homogeneous PHEMA monolayer. The drop spreads, reaches a maximum diameter, and comes to rest.

In contrast to this, an impact experiment on a homogeneous PFA monolayer is shown in figure 5. Here, the drop spreads, reaches a maximum wetted area, and after some time starts to retract. After completion of the contraction it oscillates for some time and then reaches its equilibrium shape.
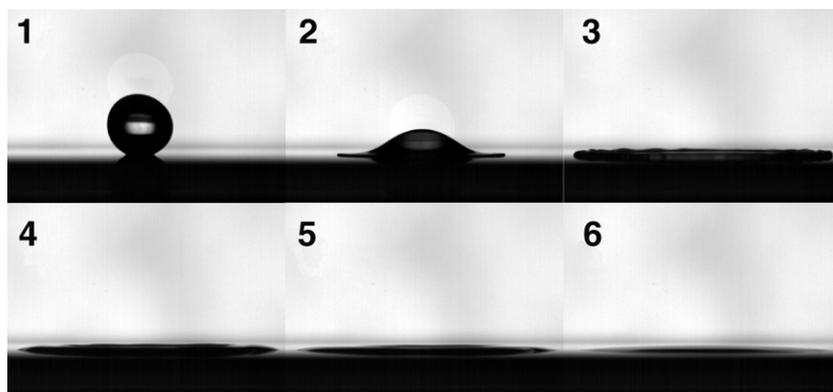
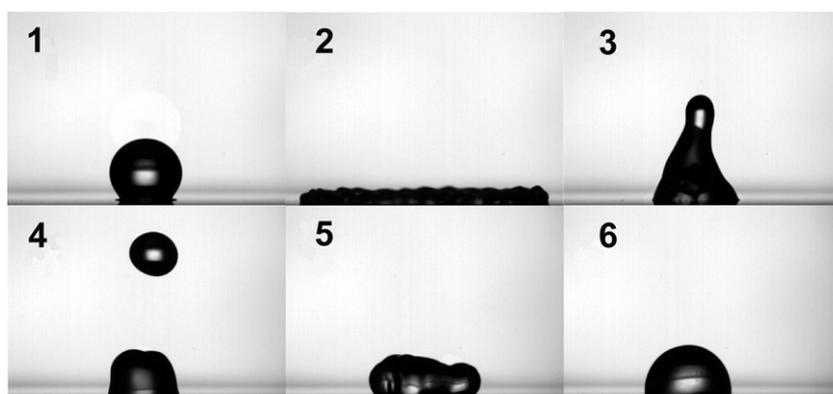**Figure 4.** Impact experiment on a homogeneously coated PHEMA substrate.

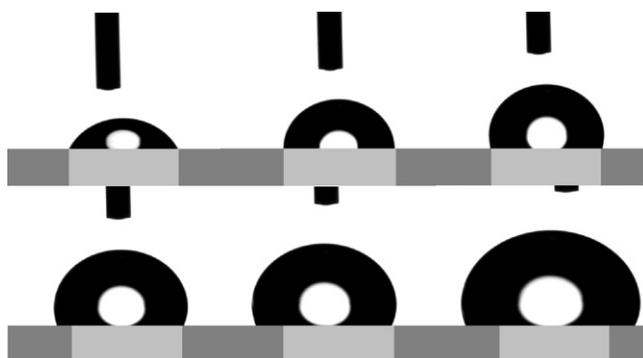**Figure 5.** Impact experiment on a homogeneously coated PFA surface.

Figure 6. Video images of water drops on a PFA coated substrate with a hydrophilic spot (light grey) of 3 mm diameter. The drop volumes used are 1, 2, 3, 4, 5 and 8 μl.

Images of water drops having various drop sizes which have been positioned on a chemically structured surface are shown in figure 6. The drops were slowly deposited on a PFA coated surface with a hydrophilic spot of 3 mm diameter. The contact angle of the
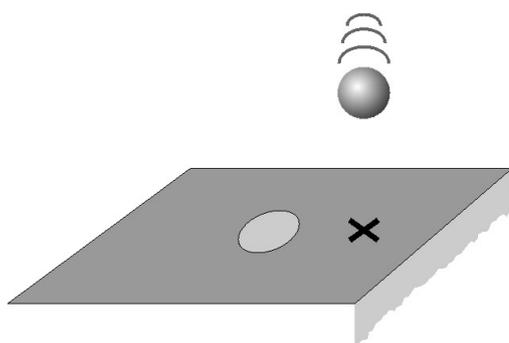
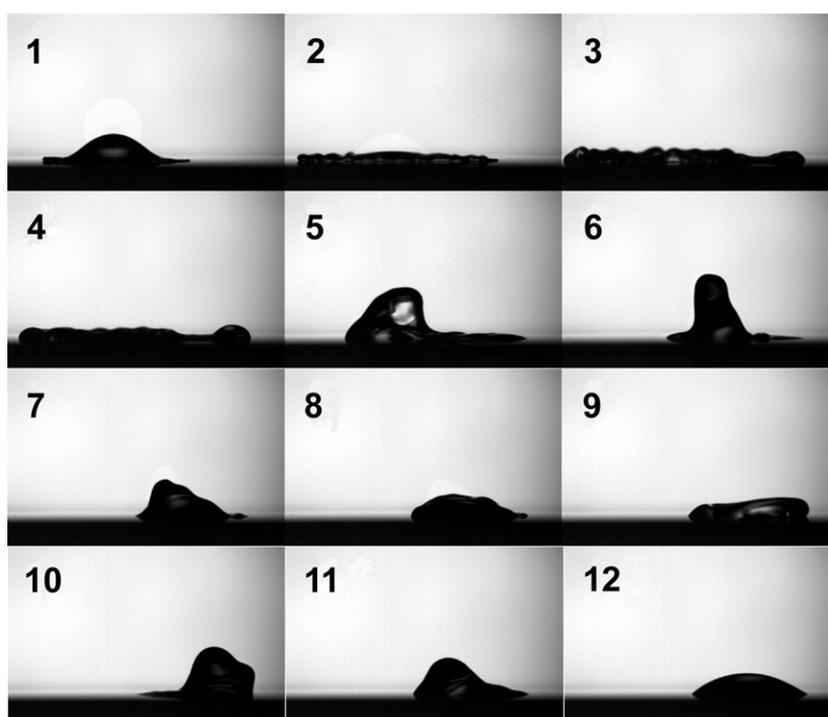**Figure 7.** The centre of the impacting drop is shifted with respect to the hydrophilic spot centre.

Figure 8. Impact experiment on a PFA coated substrate with a hydrophilic spot of 6 mm diameter. The centre of the hydrophilic spot is shifted 5 mm with respect to the impact centre.

hydrophilic substrate itself was 20°. This value was obtained from a substrate where the surface-attached polymer monolayer was completely photochemically removed. When we deposited drops, which had approximately the same size as the hydrophilic spot, we observed contact angles much higher than those on the unstructured substrate. Drops of 1, 2, 3, 4, 5 and 8 μl volumes resulted in contact angles of 60°, 90°, 105°, 109°, 111° and 111°, respectively. It should be noted that for smaller volumes the drop was pinned completely, and for larger volumes only partially to the edges of the hydrophilic spot before it finally spread onto the hydrophobic coating.
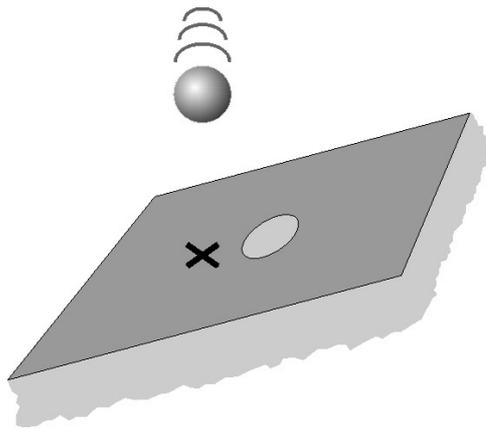
Figure 9. Drop impact on a chemically structured and inclined surface. The drop hits the surface below the centre of the hydrophilic area.
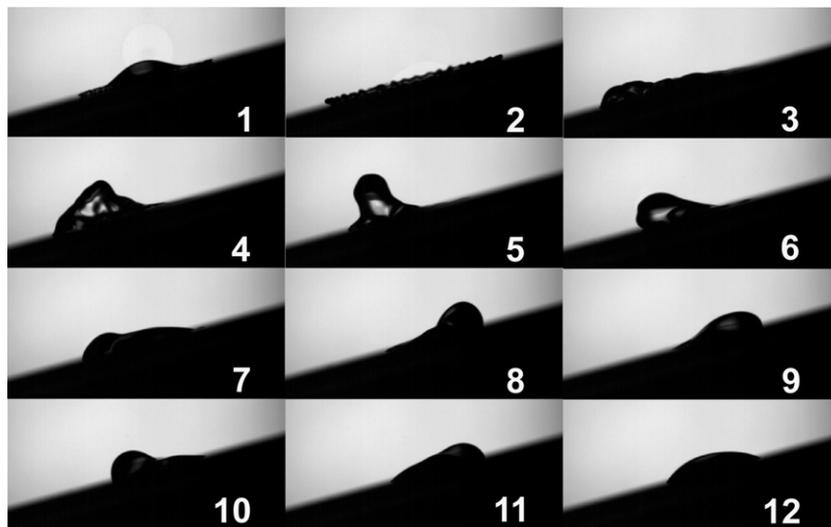

Figure 10. Impact experiment on a PFA coated surface with a hydrophilic spot of 6 mm diameter. The drop impacts 1.5 mm below the centre of the hydrophilic region. The substrate has an inclination of 15°.

The static drop deposition experiments also describe more or less correctly the situation of a central impact, where the centre of gravity of the drop is directly above the centre of the hydrophilic spot. A more detailed analysis of this situation will be published elsewhere.

If the centre of the drop is shifted with respect to the centre of the hydrophilic spot (figure 7) and the drop hits the surface with a not too small velocity, we observe a behaviour as shown in figure 8.

The drop spreads due to its kinetic energy, and finally reaches a maximum diameter. If the drop reaches the hydrophilic spot during this spreading phase, the whole drop moves in such a way that the centre of gravity of the drop reaches the hydrophilic spot. After some oscillations it eventually covers the hydrophilic spot completely.

A similar, but stronger, effect can be observed on an inclined surface (figure 9).
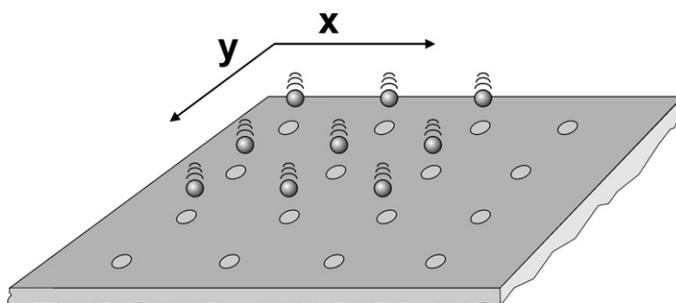
Figure 11. Impact of a series of drops onto an array. Here, the situation for central impacts is shown. The coordinate system denotes the axes, along which the drop lattice is shifted (see figures 13 and 14).
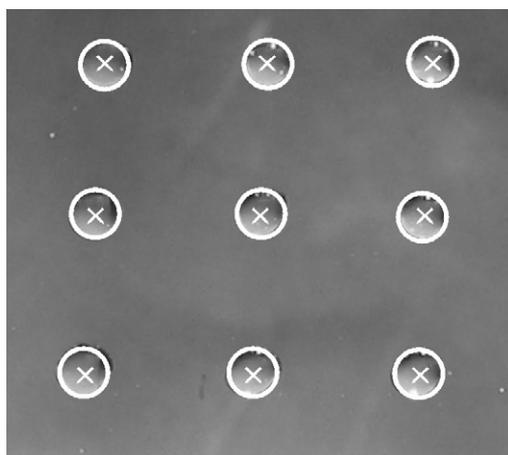

Figure 12. Photograph of an array where nine droplets impacted on nine hydrophilic spots with a diameter of 3 mm. The central impact positions are marked with a white cross.

In figure 10 we show the results for a drop impacting on a PFA coated surface 1.5 mm below the centre of the hydrophilic spot. The surface has an inclination of 15°. The drop spreads, moves down the plane, retracts, and eventually moves a little uphill to completely cover the hydrophilic spot.

Thus, the impacting drop retracts to the hydrophilic spot even for a large deviation between impact centre and hydrophilic spot centre on both even and slightly inclined substrates. Accordingly, such a self-centring effect, where the drop 'knows' its final resting position, even if it has been ejected towards the surface with a little offset, might also be useful for applications in which arrays are printed. First experiments have been performed and the results are described below.

As a model situation we observed multiple drop impacts on an array with 16 hydrophilic spots of 3 mm diameter and a spot-to-spot distance of 12 mm (figure 11).

Figure 12 shows the result for the central impact of nine drops on nine hydrophilic spots of the array. In this figure the video micrographs of the drops are superimposed with the positions where the centre of the drop impacted onto the surface and with the boundaries of the hydrophilic spot, which are of course not visible on the optical image. The impact positions
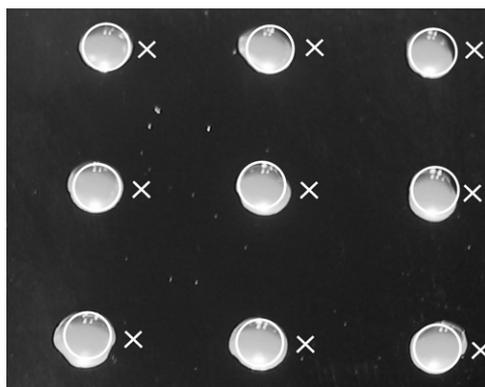
Figure 13. Photograph of an array where nine droplets impacted on nine hydrophilic spots (white rings) with a diameter of 3 mm. The impact positions had an x-offset of 2 mm (white crosses).

of the droplets are marked with a white cross, whereas the rims of the hydrophilic spots are marked with a white ring. It can be seen that the final resting position of the drops is exactly on the positions of the hydrophilic spots.

Based on the observations for single impact studies, we were interested in investigating whether a constant offset between a hydrophilic spot and the impact site influences the resulting drop pattern. This is a situation which is typical for a problem in micro-array printing, where the sample is slightly misaligned.

In figure 13 we show the results for an array where the drops had a constant offset of 2 mm with respect to the hydrophilic spot centre (see the rims of the spots versus the impact centres). It can be seen that, regardless of the misalignment, after completion of the experiment all drops sit on the 'correct' sites, i.e. on the hydrophilic spots.

As discussed above, when dispensing liquids with low surface tension, wetting of the outer surfaces of the nozzle can lead to a situation where the drop does not leave the nozzle exactly vertically, but impacts on the surface slightly off-target.

To investigate whether generating a non-wettable background for the target areas on the chip through a hydrophobic surface coating can help to overcome the problems mentioned, we chose an impact pattern where the lattice of the impacting droplets was incommensurate with the lattice of the hydrophilic spot centres (figure 14). The distances between the droplets were chosen in such a way that they were larger by a constant factor than the array spot distance. The distance between the drops in x-direction was 12 mm and the distance of the drops in y-direction 14 mm. One can see that only six out of nine drops eventually sit on hydrophilic spots, whereas three drops are positioned on the PFA coating and nearly hit the hydrophilic spots of the next row.

4. Discussion

In the first phase after impact, the shape of the drop resembles a truncated sphere [14]. During this so-called kinematic phase the wettability of the substrate is not influential. This explains why frame 3 in figure 4 and frame 2 in figure 5 look alike, despite the fact that the polymer monolayers have different wetting properties. The kinematic phase is the phase of the initial drop deformation. It is of approximate duration D_0/U_0, where D_0 denotes the initial drop diameter and U_0 the impact velocity. During this phase a radially expanding thin film, a lamella, is formed on the surface.
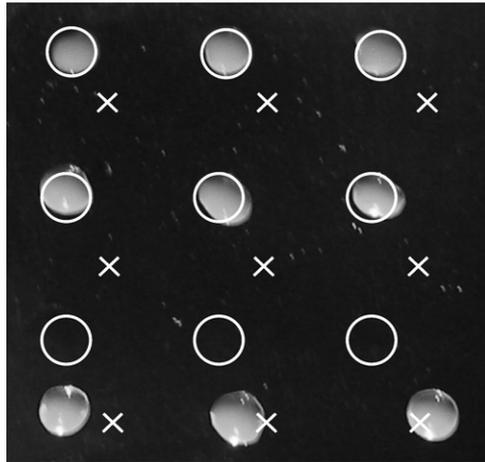
Figure 14. Photograph of an array where nine droplets impacted on the positions marked with a cross. Six out of nine droplets self-centred on hydrophilic spots. Three drops sit on the hydrophobic PFA coating.

Capillary forces at the edge of the lamella lead to the formation of a rim, whose velocity is smaller than that of the liquid in the lamella. The motion of this rim determines the evolution of the drop diameter in the following spreading and receding phase. The mass and momentum balance equations of the rim account for inertial and capillary forces, viscous drag and wettability. These equations yield the following differential equation for the radial velocity of the rim:

$$\frac{d\bar{V}_r}{dt} = \frac{12\bar{R}_r}{1 - 6\bar{R}_r^2\bar{h}_1}\left[\bar{h}_1(\bar{V}_1 - \bar{V}_r)^2 - \frac{1 - \cos\theta}{We} - \frac{6\bar{V}_r\sin\theta}{Re(1 - \cos\theta)}\right] \tag{1}$$

where the variables marked with a bar denote non-dimensional parameters obtained by the use of D_0 and U_0. $\bar{R}_r$ and $\bar{V}_r$ are the radius of the rim centreline described in a polar coordinate system with the radial coordinate r and its corresponding non-dimensional velocity. $\bar{h}_1$ and $\bar{V}_1$ are the non-dimensional thickness and velocity of the lamella and θ is the average dynamic contact angle. Re and We are the Reynolds and Weber number, respectively. The Reynolds number is defined as $Re = \rho U_0 D_0/\mu$, where ρ denotes the density and μ the viscosity of the liquid. The Weber number is defined as $We = \rho U_0^2 D_0/\sigma$, where σ denotes the surface tension of the liquid. The expressions for $\bar{h}_1$ and $\bar{V}_1$, which satisfy the mass and momentum balance in the lamella, are given by [15]

$$\bar{h}_1 = \frac{\bar{\eta}}{(\bar{t} + \bar{\tau})^2} \tag{2}$$

and

$$\bar{V}_1 = \frac{\bar{r}}{\bar{t} + \bar{\tau}}, \tag{3}$$

with $\bar{\eta}$ and $\bar{\tau}$ being non-dimensional constants, which describe the viscosity and the radius of the lamella. These can be estimated according to procedures given in Roisman *et al* [14]. Further considerations concerning the drop impact behaviour on chemically structured surfaces can be found elsewhere [9].

During the spreading phase the surface tension forces become relevant. In the case of the hydrophilic PHEMA coating, the drop is attracted by the surface and starts to spread, whereas

on the PFA surface, the drop starts to retract due to the hydrophobic coating. This continues until the equilibrium phase, in which a stable situation is reached.

For chemically structured surfaces it is known that the equilibrium contact angle depends both on the size of the drop and the structured area [16]. If the drop is small enough to only partially wet the hydrophilic domain it will exhibit the contact angle of the area where it is deposited. In our case, if the drop was small enough and/or the hydrophilic area large enough, we would observe a contact angle of 20°. However, if the drop covers the hydrophilic domain completely, Young's equation is not satisfied and the drop contact line is pinned to the boundary of the hydrophilic spot. The contact angle then increases with increasing drop volume. Even though the surface is very hydrophilic at the sites studied, contact angles of 70°–100° are reached. Only when the contact angle of the confined drop reaches the contact angle of the outer hydrophobic coating does it start to move out of the confinement. In figure 6, the contact angle of the unstructured PFA coating (111°) is reached when a drop with a volume of 4 μl is deposited. When the volume is further increased, the drop boundaries move out of the confinement, as expected, and the contact angle remains constantly the same as if there were no hydrophilic spot present.

The experiments, in which inclined and patterned surfaces are used, exemplify the strong tendency of the drop to reach an area with appropriate surface chemistry: as long as some part of the drop reaches the hydrophilic spot during the spreading phase and the surface inclination is not too strong, the drop moves automatically onto the hydrophilic spot to minimize the surface interaction with the hydrophobic coating. As the spreading of the liquid on the surface-attached monolayer can be quite strong if the drop has sufficient kinetic energy, situations can even be observed in which a drop which impacts on the surface a few drop diameters off the hydrophilic target still resides directly on target in the equilibrium position. The exact distance between the target site and impact area is expected to depend on the surface chemistry of the substrate, as the maximum size the drop assumes under given impact conditions depends on the surface energy of the substrate.

As demonstrated in figures 7 and 8, such a self-centring effect of the hydrophobic coating can help to compensate misprints during the generation of (micro-) arrays. However, there are also limitations to this self-correction mechanism. A case where the deviations between target and impact site became too large for such an automatic correction is shown in figure 9. There, the drops which are the strongest off-target, i.e. the ones in the bottom row, remain on the PFA coating or, in other cases, if the mismatch between the desired and actual impact site is so large that the drop is close enough to a neighbouring row during the spreading phase, it might even end up in the wrong row.

5. Conclusions

By using a strongly hydrophobic background for printing of arrays with hydrophilic spots it is possible to minimize or completely circumvent surface misprints. If the drop impacts on the surface slightly off-target, but in such a way that the liquid still reaches the hydrophilic target spot during the spreading phase of the impact process, the drop moves to the area where the surface energy is minimized. This is very important if a printing process is employed in which low surface energy liquids are printed through micronozzles. In this case quite frequently wetting at the outer surfaces of the nozzle can occur, which make a precise targeting in the printing process difficult.

In addition, such a self-correction process is interesting if it is desired to print several times on the same spot. This applies to cases in which surface reactions occur on (micro-) arrays. Usually printing two or more times on the same spot would require a very precise alignment

procedure. This alignment problem can be avoided if the surface chemistry of the substrate is chosen in such a way that the drops are automatically centred onto the correct position.

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