POLED displays: Robust printing of pixels

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The fabrication of a high-quality POLED (Polymeric Organic Light Emitting Diode) display requires the deposition of identical, uniform fluid films into a large number of shallow recessed regions that form a regular array of pixels on a display backplane. We determine the protocols required to achieve continuous liquid coverage of the entire pixel area for the case where equally-spaced fluid droplets are sequentially printed along a straight line within a stadium-shaped pixel, and explore how these protocols depend on the wetting properties of the pixel surface. Our investigation uses a combination of experiments and numerical modelling, based on the assumption of fluid redistribution via capillary spreading according to a Cox-Voinov law. We show that the model is able to predict quantitatively the evolution of the liquid deposited in a pixel and provides a computationally inexpensive design tool to determine efficient printing strategies that account for uncertainties arising from imperfect substrate preparation or printhead dysfunction.

In recent years, inkjet printing-based manufacturing has established itself as a simpler and more economical approach than conventional lithography processes for the production of a variety of microelectronics displays, sensors, photovoltaic cells, etc. However, limitations pertaining to the stability of functionalized inks and the need for robust printing strategies that will yield controlled thin-film deposits of non-trivial shapes, mean that the technology has had limited uptake on an industrial scale. In this letter, we explore printing strategies that can be used to form an elongated thin-film (L ≈ 200 μm) of specified shape by sequential deposition of partially overlapping droplets; a process which arises in the context of POLED (Polymeric Organic Light Emitting Diode) display fabrication.

The manufacture of high-resolution POLED displays via inkjet printing requires the controlled deposition of a dense pattern of identical liquid films of a functional material in solution. Solid deposits are formed upon evaporation of the solvent to yield the bottom-gated transistors that emit light, commonly referred to as pixels. The formation of continuous solid deposits, which is essential to achieve high-performance displays, requires the coverage of the entire pixel area by the deposited liquid film. In addition, an accurately defined pixel edge is required in order to deter unwanted leakage currents and crosstalk between the pixels. This is a considerable challenge for the inkjet-printing of thin-films which tends to suffer from low spatial resolution. Hence, chemical or geometric substrate patterns are commonly introduced to manipulate the spreading of the deposited liquid. Kant et al recently identified the distinct roles of topography and wettability patterning in the sequential deposition of partially overlapping droplets within a shallow recessed substrate region (pixel) that was highly wetting compared to the elevated banks surrounding it. They found that the presence of bounding side walls enhances local spreading thus facilitating fluid coverage of the entire recessed region, whereas wettability patterning ensures containment of the fluid within the pixel. Hence, robust filling of pixels requires both forms of patterning in combination.

In this letter, we focus on determining the conditions required to fill such pixels as a function of the wetting properties of the substrate and the printing parameters, i.e. the total number of droplets deposited in a pixel (N) and the inter-drop distance between them (Δx). We demonstrate that a simple model based on capillary spreading of the deposited liquid provides a computationally inexpensive design-tool to determine safe printing strategies that account for experimental limitations pertaining to the patterning accuracy and printhead operation.

Experimental methods: A schematic diagram of the experimental setup is shown in Fig. 1a. The details of the experimental setup have been described elsewhere and thus we will only give a brief description of the points most pertinent to the present study. In a typical experiment equidistant partially overlapping droplets (each of volume V = 7.6 ± 0.4 pL) were deposited onto a substrate using a horizontally translating drop-on-demand inkjet printhead (SX3, Fujifilm Dimatix) at a constant frequency of f = 80 Hz. Drops produced from the printhead had an in-flight radius Rf = 12.2 μm and coalesced with the pre-existing fluid layer upon impact. The printhead was moved horizontally at different speeds v using a linear motion stage (ANT95L, Aerotech) to vary the inter-drop distance (Δx = v/f) between neighbouring droplets. The fluid was a Cambridge Display Technology (CDT) proprietary solution used in POLED printing with dynamic viscosity η = 6.25 × 10⁻³

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Pa s, density ρ = 1.066 × 10^3 kg m⁻³ and surface tension σ = 44 × 10⁻³ N m⁻¹. The Weber number of the droplet impact was low, \( We = 2 \rho V_i^2 R_i / \sigma = 2.4 \), where \( V_i = 2.2 \) m s⁻¹ is the vertical velocity of the droplet\(^{20}\), and accordingly no splashing was observed at the time of impact\(^{28}\). We report observations based on the bottom views recorded at 500 frames per second.

Experiments were performed on sample display backplanes manufactured in the clean room facility of CDT, each having a pixel density of 200 pixels per inch – see Kant et al.\(^{27}\) for details of the fabrication process and techniques used for the characterisation of the topographical and wettability patterns. Each pixel on the display consisted of a recessed stadium-shaped well bound by 1.2 μm high sloping side walls (i.e. 10% of the in-flight droplet radius), with different wetting properties inside (\( 4^\circ \leq \theta_{Ai} \leq 40^\circ \), \( \theta_{Ri} = 0^\circ \)), on the narrow sloping walls (\( \theta_{Aw} = 47^\circ \), \( \theta_{Rw} = 0^\circ \)) and outside (\( \theta_{Ao} = 65 \pm 2^\circ \), \( \theta_{Ro} = 40 \pm 2^\circ \)) the pixel boundary; here \( \theta_{Ai} \) and \( \theta_{Ri} \) refer to the advancing and receding contact angles, respectively; see ESI. We varied the inner advancing contact angle by letting the substrate age in the laboratory; this aging did not affect the contact angles on the walls and outer surfaces which remained approximately constant. The high values of the advancing and receding contact angles on the banks surrounding the pixels ensured that any droplet deposited partially outside the boundary retreated into the pixel so that the deposited volume was contained inside the pixel\(^{27}\).

**Numerical model:** The details of the model development have also been presented previously\(^{20,26,27}\). Briefly, we model the deposited liquid mass as a thin film of fixed volume that evolves through (quasi-static) capillary effects. A kinematic boundary condition advances the contact line according to a Cox-Voinov spreading law\(^{29,30}\), which we parameterise using the experimental contact-angle measurements to give a wetting profile for the pixel, see Fig. 2. The only initial conditions required for the model are the total volume and the footprint shape of the wetted region. Upon deposition of a new droplet, the liquid footprint is taken as the union of the regions wetted by the existing liquid morphology and by the newly deposited droplet, and the total volume is incremented accordingly. The fluid pressure and height profile consistent with the updated footprint and fluid volume are then adjusted to ensure that the fluid is in static equilibrium. This model was implemented numerically using the finite element library oomph-lib\(^{31}\), see source code\(^{32}\) and ESI for model details.

The three sequences of images in Fig. 1 illustrate the evolution of a liquid line formed from the deposition inside a pixel of seven equidistant droplets, thus a fixed volume of fluid, for different values of pixel wettability (\( \theta_{Ai} \)) and inter-droplet spacing (\( \Delta x \)). The centre of the initial droplet was always located at a distance of \( \Delta x = 14 \pm 3 \) μm from the edge of the pixel. In all three cases, the droplet deposition leads to the formation of a rivulet that fills the pixel at the upstream end and narrows as further droplets are deposited downstream. The three liquid lines evolve towards distinct equilibrium configurations (last image in each sequence), with only Fig. 1b resulting in a filled pixel. In Fig. 1b, the pixel does not fill because of the increased advancing contact angle on the inner pixel surface (\( \theta_{Ai} = 38^\circ \)). In Fig. 1c,d, the value of \( \Delta x \) has been chosen so that the liquid line extends over the whole length.
of the pixel ($\Delta x = 35 \, \mu m$) in contrast with Fig. 1, where $\Delta x = 25 \, \mu m$. Although in Fig. 1 the contact angle is low ($\theta_{AI} = 20^\circ$), the pixel does not fill because the line of deposited fluid does not extend to the end of the pixel (and the wetting front propagating along the pixel boundary comes to rest when it reaches the end of the liquid line).

The red contours overlaid on the experimental snapshots in Fig. 2 represent the footprints of the deposited liquid computed numerically for the same parameter values as in the experimental sequences. The model captures the main features of the evolution of the liquid lines for different values of $\theta_{AI}$ and $\Delta x$. At early times ($t \leq 0.0875 \, s$), the model predictions are almost indistinguishable from the experiment. Small discrepancies in the position of the wetting fronts along the side-walls occur only in Fig. 2a, which we attribute to experimental variability in the wetting properties of the side-walls (see Fig. 2 for further discussion). At later times, the liquid spreads faster in the computations because the model does not include any viscous effects which begin to restrict the flow in the experiments. Despite the difference in the spreading time scales, the model correctly predicts the evolution and the equilibrium states of the three liquid lines in Fig. 2.

![FIG. 2. Example of an anomalous experimental equilibrium footprint obtained following the deposition of five droplets ($\Delta x = 35 \, \mu m$) with their centroids displaced from the horizontal centreline of the pixel by $5\%$ of the pixel width ($\theta_{AI} = 30^\circ$). The contact line does not extend to the side walls of the pixel, suggesting that the inner-surface of the pixel is bound by a non-wetting region. This experimental footprint is compared with numerical simulations performed for (a) the wetting profile used throughout this paper (yellow contour); (b) a profile where the region with $\theta_{AI} = 47^\circ$ has been extended into the flat recessed portion of the pixel (red contour). In the wettability profiles, $B$ denotes the local height of the pixel, with $B = 0$ inside the pixel, and $\theta_L$ is the advancing contact angle.

The examples shown in Fig. 1 demonstrate that the filling of pixels does not occur for all values of $\theta_{AI}$ and $\Delta x$. A large number of experiments ($\sim 100$) were conducted to construct a phase diagram of ‘filled’ or ‘partially filled’ equilibrium states in terms of the operating conditions ($N, \Delta x$) for pixels of three different wettabilities $\theta_{AI} = 4.5^\circ, 20^\circ$ and 38$^\circ$. The resulting phase diagram is shown in Fig. 3. The shaded region indicates conditions for which at least one droplet is deposited entirely outside the pixel, while the filled circles interpolated by solid lines represent the minimum number of droplets required to fill a pixel as a function of inter-drop distance, for different values of $\theta_{AI}$. Thus, the areas above each threshold boundary that are bordered by the red-shaded region on the right-hand-side correspond to the ‘safe’ operating conditions that systematically lead to filled pixels. Note that the boundaries between different regions in the phase diagram were determined experimentally.

For wetting pixels ($\theta_{AI} = 4.5^\circ$), ‘safe’ operating conditions are for $N \geq 4$ (green line) because the low contact angle enables the line to spread to the end of the pixel regardless of droplet positioning. This means that the filling of a wetting pixel only depends on the total volume deposited; see Figs. S4 and S5. The number of droplets required to fill the pixel decreases with decreasing contact angle until for strongly wetting substrates ($\theta_{AI} < 1^\circ$) a single droplet can fill the pixel provided that the volumetric evaporation rate is not too high.

For partially wetting substrates ($20^\circ \leq \theta \leq 38^\circ$), the filling of a pixel for small values of $\Delta x$ also requires the volume deposited to exceed a threshold value. However, the number of droplets required to fill the pixel decreases as the inter-drop distance increases (blue line: $\theta_{AI} = 20^\circ$; black line: $\theta_{AI} = 38^\circ$) because the filling of the pixel relies on the liquid line reaching the downstream end of the pixel and this can be achieved for a reduced total deposited volume by increasing $\Delta x$. This result is consistent with Fig. 1b, where at $\Delta x = 35 \, \mu m$, the liquid line extends over the length of the pixel and the side walls enhance spreading sufficiently to fill the pixel. Overall, the area of the parameter plane that leads to filled equilibrium states shrinks with increasing $\theta_{AI}$. However, the minimum number of droplets required to fill the pixel can be reduced by using droplets of higher volume, thus expanding the safe range of operating conditions; see Fig. S6.

Using the numerical model, we were able to reproduce the threshold operating conditions that separate filled and partially filled pixel states; see Fig. 3. The numerical model systematically reproduces the details of the equilibrium configurations observed in the experiments, and hence predicts the boundary between filled and under-filled pixels. This agreement demonstrates the utility of our computationally inexpensive model, promoting it as a feasible design tool for inkjet-printing-based manufacturing.

In a small subset of experimental pixels, anomalous equilibrium configurations were obtained, which the model used in Figs. 1 and 3 failed to capture. An example is shown in Fig. 2 where the off-centred deposition of five droplets yields an equilibrium liquid line that does not extend to the side walls. The footprint calculated numerically with the wetting profile used so far, differs from the experiment in that one side of the footprint has spread along the bounding wall, as indicated by the presence of a wetting front (Fig. 2a). We find that a change in the imposed wetting profile can reproduce the exper-
FIG. 3. Phase diagram summarizing the influence of the inner advancing contact angle $\theta_{Ai}$ and the printing protocol $(N, \Delta x)$ on the filling of a stadium-shaped pixel. The boundary of the red-shaded region represents the maximum number of droplets which can be deposited at least partially inside the pixel for a chosen value of $\Delta x$. The filled circles, linearly interpolated by solid lines, correspond to the threshold operating conditions that separate filled and partially filled pixels with $\theta_{Ai} = 4.5^\circ$ (green), $20^\circ$ (blue) and $38^\circ$ (black), respectively. Each data point indicates three concurrent experiments, and the accuracy of each data point was confirmed by performing repeated experiments for one and two fewer droplets as well as for one more droplet, which consistently led to partially filled and filled pixels, respectively. Hence, safe operating conditions that result in a filled pixel are in the regions above the threshold conditions and left of the red-shaded region. The stars correspond to the operating conditions of the snapshots on the right side of the graph for $\theta_{Ai} = 20^\circ$; $38^\circ$, and in the ESI for $\theta_{Ai} = 4.5^\circ$. The red contours are the numerically computed equilibrium footprints for the same parameter values.

mental equilibrium state numerically (Fig. 2b): the region where $\theta_{Aw}(\theta_{Rw}) = 47^\circ(0^\circ)$ is extended by 0.5 $\mu$m (1.5% of the pixel width) into the inner pixel region. This result suggests that the numerical model can be used to diagnose small variations in the wetting properties of the side-walls across pixels, which result from the fabrication process. This known variability in the wetting profile can in turn be accounted for when numerically predicting safe operating conditions that lead to filled pixels.

Finally, we used the numerical model to capture the effect of a printhead dysfunction commonly encountered during operations on an industrial scale, namely the misfiring of a droplet. As printing defects can lead to partially filled pixels, which reduce the overall resolution and performance of a display device, it is necessary to account for such dysfunctions at the design stage. In Fig. 4, a numerical scheme is depicted which misses out the printing of the penultimate droplet, in order to account for the misfiring of a droplet during the deposition sequence. Experimental and numerical equilibrium configurations obtained following this protocol are in excellent agreement. This test suggests that the numerical model may be used to identify a subset of the safe operating conditions reported in Fig. 3 where filling is ensured despite the occasional misfiring of the printhead.

To summarize, we have discussed various aspects pertaining to the printing of short liquid lines to robustly fill pixels in the context of POLED display fabrication. We have shown that in order for sequentially deposited droplets that coalesce upon impact to form a thin film that covers the entire pixel surface, the wettability of the pixel surface must be considered in conjunction with the deposition parameters. Furthermore, we have demonstrated that a simple model that relies on capillary spreading according to a Cox-Voinov spreading law can be used as a computationally inexpensive design tool to determine efficient printing strategies in the fabrication of high performance POLED and also LCD (Liquid Crystal Display) devices.

1. P. Calvert, Chem. Mater. 13, 3299 (2001).
2. M. Singh, H. M. Haverinen, P. Dhagat, and G. E. Jabbour, Adv. Mater. 22, 673 (2010).
3. H. Sirringhaus, T. Kawase, R. Friend, T. Shimoda, M. Inbasekaran, W. Wu, and E. Woo, Science 290, 2123 (2000).
4. H. Minemawari, T. Yamada, H. Matsui, J. Tsutsumi, S. Haas, R. Chiba, R. Kumai, and T. Hasegawa, Nature 475, 364 (2011).
5. S. H. Ko, H. Pan, C. P. Grigoropoulos, C. K. Lucombe, J. M. Fréchet, and D. Poulikakos, Nanotechnology 18, 345202 (2007).
6. P. Andersson, R. Forchheimer, P. Tehrani, and M. Berggren, Adv. Funct. Mater. 17, 3074 (2007).
7. T. Shimoda, K. Morii, S. Seki, and H. Kiguchi, MRS Bull. 28, 821 (2003).
8. J. Halls, in Inf. Disp., Vol. 2 (2005).
9. V. Dua, S. P. Surwade, S. Ammu, S. R. Agnihotra, S. Jain, K. E. Roberts, S. Park, R. S. Ruoff, and S. K. Manohar, Angew. Chem. 122, 2200 (2010).
10. P. Lorwongtragool, E. Sowade, N. Watthanawisuth, R. R. Baumann, and T. Kerdcharoen, Sensors 14, 19700 (2014).
11. K. Abe, K. Suzuki, and D. Citterio, Anal. Chem. 80, 6928 (2008).
12. C. N. Hoth, P. Schilinsky, S. A. Choulis, and C. J. Brabec, Nano Lett. 8, 2806 (2008).
13. S. Jung, A. Sou, K. Banger, D.-H. Ko, P. C. Chow, C. R. McNeill, and H. Sirringhaus, Adv. Energy Mater. 4, 1400432 (2014).
14. J. Stringer and B. Derby, Langmuir 26, 10365 (2010).
15. P. C. Duineveld, J. Fluid Mech. 477, 175 (2003).
16. A. Dalili, S. Chandra, J. Mostaghimi, H. C. Fan, and J. C. Simmer, J. Colloid Interf. Sci. 418, 292 (2014).
17. E. Sowade, K. Y. Mitra, E. Ramon, C. Martínez-Domingo, F. Villani, F. Loffredo, H. L. Gomes, and R. R. Baumann, Org. Electron. 30, 237 (2016).
18. J. Noh, M. Jung, Y. Jung, C. Yeom, M. Pyo, and G. Cho, Proc. IEEE 103, 554 (2015).
19. D. Soltman and V. Subramanian, Langmuir 24, 2224 (2008).
20. A. B. Thompson, C. R. Tipton, A. Juel, A. L. Hazel, and M. Dowling, J. Fluid Mech. 761, 261 (2014).
21. J. Wang, Z. Zheng, H. Li, W. Huck, and H. Sirringhaus, Nat. Mater. 3, 171 (2004).
22. H. Gau, S. Herminghaus, P. Lenz, and R. Lipowsky, Science 283, 46 (1999).
23. M. Kuang, L. Wang, and Y. Song, Adv. Mater. 26, 6950 (2014).
24. C. E. Hendriks, P. J. Smith, J. Perelaer, A. M. Van den Berg, and U. S. Schubert, Adv. Funct. Mater. 18, 1031 (2008).
25. R. Seemann, M. Brinkmann, E. J. Kramer, F. F. Lange, and R. Lipowsky, Proc. Natl. Acad. Sci. 102, 1848 (2005).
26. P. Kant, A. L. Hazel, M. Dowling, A. B. Thompson, and A. Juel, Phys. Rev. Fluids 2, 094002 (2017).
27. P. Kant, A. L. Hazel, M. Dowling, A. B. Thompson, and A. Juel, Soft matter 14, 8709 (2018).
28. C. W. Visser, P. E. Frommhold, S. Wildeman, R. Mettin, D. Lohse, and C. Sun, Soft Matter 11, 1708 (2015).
29. R. Cox, J. Fluid Mech. 168, 169 (1986).
30. O. Voinov, Fluid Dyn. 11, 714 (1976).
31. M. Heil and A. L. Hazel, in Fluid-structure interaction (Springer, 2006) pp. 19–49.
32. https://figshare.com/s/9e95e92400ee8e74e6ac.
33. C.-T. Chen, K.-H. Wu, C.-F. Lu, and F. Shieh, J. Micromech. Microeng. 20, 055004 (2010).