Control of drop positioning using chemical patterning

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We explore how chemical patterning on surfaces can be used to control drop wetting. Both numerical and experimental results are presented to show how the dynamic pathway and equilibrium shape of the drops are altered by a hydrophobic grid. The grid proves a successful way of confining drops and we show that it can be used to alleviate mottle, a degradation in image quality which results from uneven drop coalescence due to randomness in the positions of the drops within the jetted array.

From microfluidic technology to detergent design and ink-jet printing it is important to investigate the way in which drops move across surfaces. The dynamics of the drops will be affected by any chemical heterogeneities on the surface \cite{1, 2, 3}. Until recently such disorder was usually regarded as undesirable. However with the advent of microfabrication techniques it has become possible to control the chemical patterning of a substrate down to nanoscale, leading to the possibility of exploring how such patterning can control, rather than disturb, drop motion.

A practical example where such an approach might be of use is in ink-jet printing. Although ink-jet printers are widely available for domestic use the quality of the images is still not sufficiently robust to allow widespread industrial applications. The possibility of replacing the traditional contact techniques with electronically controlled template design, particularly for small print runs, is highly desirable for both efficiency and cost.

In the printed image a patch of colour is produced by jetting drops in a regular, square array. The closer the drops the more intense the colour of the patch appears to the eye. To achieve a solid colour the aim is that drops jetted at a distance apart comparable to their diameter should coalesce and form a uniform covering of ink. However, in practice, randomness in the positions at which the drops land, combined with surface imperfections, often lead to local coalescence and the formation of large, irregular drops with areas of bare substrate between them as shown in fig. \textsuperscript{4}a) and the upper part of fig. \textsuperscript{4}b) such configurations are likely to lead to poor image quality, called mottle \textsuperscript{4}.

In an attempt to overcome this problem we demonstrate how using a two-dimensional array of hydrophobic chemical stripes can be used to control the equilibrium shape, the position and the dynamic pathway of spreading drops. The hydrophobic stripes form barriers controlling the drops and allowing their relative positions to be tuned. The behaviour of single drops, and then an array of drops on the patterned surfaces, is explored both by solving the hydrodynamics equations of motion by means of a lattice Boltzmann algorithm and by performing suitable experiments.

In the numerical modelling we consider a liquid-gas system of density $n(r)$ and volume $V$. The surface of the substrate is denoted by $S$. The equilibrium properties of the drop are described by the free energy

$$\Psi = \int_V \left( \psi_b(n) + \frac{\kappa}{2} (\partial_\alpha n)^2 \right) dV + \int_S \psi_s(n) dS$$ (1)

where Einstein notation is understood for the Cartesian label $\alpha$ and where $\psi_b(n)$ is the free energy in the bulk which we take to have a Van der Waals form. The derivative term in equation (1) models the free energy associated with density gradients at an interface. $\kappa$ is related to the surface tension. Following Cahn \textsuperscript{5} we choose $\psi_s(n_s) = -\phi_1 n_s$, where $n_s$ denotes the density at the surface, to control the wetting properties at the fluid.

We use a lattice Boltzmann model to solve the Navier-Stokes equations of this liquid-gas system

$$\partial_t (n \mathbf{u}_\alpha) + \partial_\beta (n \mathbf{u}_\alpha \mathbf{u}_\beta) = - \partial_\beta P_{\alpha\beta} + \nu \partial_\beta [n (\partial_\beta \mathbf{u}_\alpha + \partial_\alpha \mathbf{u}_\beta + \delta_{\alpha\beta} \partial_\gamma \mathbf{u}_\gamma)],$$

$$\partial_t n + \partial_\alpha (n \mathbf{u}_\alpha) = 0$$ (2)

where $\mathbf{u}(r)$ is the fluid velocity and $\nu$ the kinematic viscosity. The pressure tensor $P_{\alpha\beta}$ incorporates information about the free energy \textsuperscript{5}. Details of the numerical algorithm can be found in \textsuperscript{6}. No slip boundary conditions on the velocity are set on all surfaces. In what follows we consider ink droplets of viscosity $\eta = 2.5 \cdot 10^{-2}$ kgm$^{-1}$s$^{-1}$ and surface tension $\sigma = 2 \cdot 10^{-2}$ Nm$^{-1}$.

The final state of a drop of liquid placed on a solid surface depends on the wetting properties of the surface \textsuperscript{7}. These are best characterised by the contact angle $\theta$ (which can be controlled in our simulations by choosing an appropriate $\phi_1$). Drops prefer to lie on hydrophobic surfaces, while hydrophilic ones have a contact angle $\theta_{\phi_0} = 65^\circ$ on a substrate which otherwise has a contact angle $\theta_{\phi_0} = 5^\circ$. Fig. \textsuperscript{7} shows the behaviour of drops of radius $R = 15 \mu m$ which are placed on such surfaces so that they are initially just touching the surface at the point marked with a black dot. Thin lines on the figures
show how the drop spreads in time and thick lines show the final shape. The figures compare different spacing between, and width of, the grid lines and different impact points of the drop.

We first consider, in fig. 1(a), stripes of width 6\(\mu\)m spaced by 40\(\mu\)m. In this case the hydrophilic area is too small compared to the drop volume to confine the drop within a single square (the south-west drift is due to the impact point being set slightly off centre). Fig. 1(b) shows that increasing the spacing between the stripes to 66\(\mu\)m creates an hydrophilic region big enough to confine the drop. Surprisingly this is true for any point of impact within the hydrophilic square as illustrated in fig. 1(c) where the drops lands in the corner of the square.

The confinement occurs because the surface tension penalty, which results from the final shape of the drop being non-spherical, is outweighed by the advantage of not having to lie on the hydrophobic regions of the surface. For thinner hydrophobic stripes, 4\(\mu\)m, shown in fig. 1(d), the free energy penalty is smaller and hence the driving force for confinement is less and the drops takes an extra 0.7ms to be pulled back into its original square.

We consider two surfaces (a) and (b) on which an array of drops, in approximate registry with the hydrophobic grid. Our aim is to show how chemical patterning can be used to address the problem of mottle, uneven droplet coalescence, that can severely limit image quality in ink jet printing.

We now turn to consider the behaviour of an array of drops landed on the hydrophobic grid. The random nature of the loading is however set by adding noise. Fig. 2 also shows non-wetted regions along the inner hydrophobic stripes.

The confined drops show strong confinement (but within four squares, because the relative sizes of drop and grid are larger than in the simulation). The equilibrium shape reflects the underlying patterning. Fig. 2 also shows non-wetted regions along the inner hydrophobic stripes.

We now consider the behaviour of an array of 15\(\mu\)m radius drops jetted at 3ms\(^{-1}\). Surface (a) is homogeneous with an equilibrium contact angle \(\theta_{\text{phi}} = 5^\circ\) whereas surface (b) is patterned by vertical and horizontal stripes of contact angle \(\theta_{\text{pho}} = 65^\circ\). Stripes are regularly spaced every 68\(\mu\)m and are 5\(\mu\)m wide. In the areas between the stripes, the contact angle \(\theta_{\text{phi}} = 5^\circ\).

The drops are jetted so as to hit the surface at approximately the middle of each hydrophilic square. Randomness in the position of impact is however set by adding a \(\pm 5\mu\)m noise. Fig. 3 shows the spreading of drops with and without chemical patterning.

Fig. 3(a) shows that, on substrate (a), the randomness of the drop impact points produces an uneven and complicated pattern. The drops which land slightly closer together coalesce first and immediately start to dewet the surrounding substrate as they minimise their free energy by forming a larger spherical drop. This process results in larger, randomly spaced, isolated drops, with undesirable areas of bare substrate between them.

In contrast, on substrate (b), the evolution starting from identical initial condition shows that a hydrophobic grid can control the final drop position. Drops do not coalesce and form a regular array. The coverage is higher and is likely to lead to a better image quality.

FIG. 1: Time evolution of drops jetted onto substrates patterned by grids. Hydrophobic and hydrophilic areas are dark grey stripes (\(\theta_{\text{pho}} = 65^\circ\)) and white areas (\(\theta_{\text{phi}} = 5^\circ\)) respectively. Black dots are impact points. Thin lines show how the drop spreads in time and thick lines show the final shape. The droplet radius is 15\(\mu\)m. Equilibrium is reached after (a-c) 2ms, (d) 2.7ms. (a) Hydrophobic stripes width \(w = 6\mu\)m and distance between centre of stripes \(d = 40\mu\)m. The square is too small and the drop escapes. (b) \(w = 6\mu\)m and \(d = 66\mu\)m. The drop is confined. (c) \(w = 6\mu\)m and \(d = 66\mu\)m. The drop is pulled back and confined despite landing at the corner of a square. (d) \(w = 4\mu\)m and \(d = 66\mu\)m. Thinner stripes slow down the confinement process. Figures are labeled in \(\mu\)m.

FIG. 2: An ink drop spread over a chemically patterned surface. Light and dark grey areas correspond to hydrophobic (\(\theta_{\text{pho}} = 65^\circ\)) and hydrophilic (\(\theta_{\text{phi}} = 5^\circ\)) regions respectively. The drop radius is 30\(\mu\)m.

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An experiment presenting a similar situation is shown in fig. 4. The ink drops have a radius $R = 30\mu \text{m}$ and they are jetted in a $50\mu \text{m} \times 50\mu \text{m}$ array. In the upper part of the figure there is no hydrophobic grid and a mottled final drop configuration is observed. The configuration is equivalent to the second frame in fig. 3(a) because the drops are cured before reaching their final equilibrium state. There are also likely to be surface heterogeneities which may pin the drop.

This is no longer the case when the underlying surface is patterned. The lower part of fig. 4 carries hydrophobic stripes of width $5\mu \text{m}$ forming squares of side $40\mu \text{m}$. The drops now form a more regular array determined by the grid. We note that each drop covers four grid squares, as the drop radius to square side length ratio is larger than in the simulations.

In this letter we have demonstrated, both numerically and experimentally, that the chemical patterning of a substrate is surprisingly effective in controlling drop positions on a substrate. In particular the tendency of an array of drops with small randomness in their points of impact at the substrate to mottle can be controlled. It may be possible to exploit this technique to improve the quality of ink-jet images.

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