

The Behaviour of Nematic Liquid Crystals in Chemically Patterned Millimetre-Sized Rectangular Surfaces

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Abstract

We describe a method to produce nematic liquid crystal ‘semi-droplets’ with potential use in sensing by chemically patterning rectangles on solid surfaces, surrounded by a hydrophobic monolayer to confine the liquid crystal. The substrate has directional planar anchoring, while the top surface is a liquid crystal/air interface. The effects of varying the semi-droplet of E7 height between $\sim 20 - 420\mu\text{m}$; aspect ratios between 0.5 - 1; widths between 6 - 13mm, and lengths between 6 - 20mm were investigated, significantly extending the range of semi-droplets considered in the literature; their increased size is expected to be useful in real-life devices. A geometric model for the semi-droplet was derived and compared with an existing theoretical model, offering a simple method to predict the semi-droplet interface angle, which can subsequently be used to predict the maximum height and height variation along the semi-droplet. Polarized light imaging was used to deduce the semi-droplet height profile using the liquid crystal’s birefringent properties, with excellent agreement with the model for heights $\lesssim 50\mu\text{m}$, even when the semi-droplet width was larger than E7’s capillary length. It is suggested that the confinement surface is reusable by washing with the relatively cheap and safe solvent isopropanol.

Keywords

Nematic Liquid Crystal, Confinement, Reusable, Capillary Length, Air/NLC Interface, Semi-Droplet

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Introduction

A growing number of liquid crystal based sensors(1), most coming after the seminal work of Gupta *et al.*(2), are being proposed because of their fast-responding, sensitive detection potential, many of which make use of nematic liquid crystals (NLC) as birefringent fluids that exhibit orientational order over relatively large distances. Such sensors typically rely on the effect whereby a small perturbation at the surface of bulk NLC, such as the interaction of an analyte, can cause a change in the director field that is readily observed under polarised light. There are some excellent reviews that summarise recent liquid crystal sensor literature(3-5). Some recent examples of common confinement geometries of NLC in such sensors include droplets(6-16); in a NLC cell(17-22), or the NLC in contact with aqueous solutions(23-28). Some other liquid crystal-based sensing examples reported include the use of whispering gallery mode resonances(29), or polymer-stabilized NLC(30). The confinement shapes in this work are rectangles with aspect ratios between 0.5 – 1, however a review that describes the effect of varying confinement geometries is given by Shin *et al.*(31). Work on confinement of NLCs in rectangle-like geometries has been considered both experimentally and theoretically(32-40).

The motivation for investigating the confinement behaviour in this work is to explore the potential of a polarized light imaging-based NLC sensing device fabricated using carefully designed, ‘semi-droplets’ of NLC constrained onto a substrate, with one open-to-air surface. Figure 1 shows the confinement shape for the method presented in this work which uses rubbed polyimide^{1*} to produce a directional, planar alignment layer, together with contact photolithography using a bespoke photomask to define a wide range of rectangular shapes with known dimensions. A hydrophobic monolayer contains the NLC with the top

^{1*} Nissan Chemical Industries Ltd. Data sheet for “Alignment Coatings for LCDs-SUNEVER Series” -1/2

surface open to air at ambient pressure. Such an approach has potential as a simple-to-use sensor, without the need for complex geometries or microdroplet fabrication that are a feature in many other cases. The reusability of the patterning surfaces in this work, which can be suggested due to a lack of significant change in the sample quality after washing with the relatively inexpensive and non-hazardous solvent isopropanol (IPA), is then a step towards cheaper and more sustainable NLC-based sensing methods. However, the ability to understand the effect of varying the confinement dimensions and height of the confined NLC is important to the design; that is the focus of this work.

FIGURE 1 NEAR HERE

The recent papers by Bao *et al.*(38) and Cousins *et al.*(39) form the motivation for our current work. Bao *et al.*(38) produced stripes using a direct-write laser, O₂ plasma etching and deposition of a self-assembled monolayer, with no specific alignment layer on the LC-containing area. Cousins *et al.*(39) utilised rubbed poly(vinyl alcohol) (PVA) as an alignment layer, with confinement created from Teflon surrounding the rectangle. In Bao *et al.*, the stripes are 10 - 30 μ m in width (with a height for the 30 μ m stripes of 1.22 μ m), which is of a different order of magnitude to that in Cousins *et al.* who employ a width : length of 1.2 : 60mm. Both studies use geometries that are much less than the capillary length of the nematic liquid crystals used. Bao *et al.* consider a single semi-droplet height, while Cousins *et al.* record two situations of \sim 1 μ L and 3 μ L NLC dispense volumes into their confinement area. Bao *et al.* present an equation for the maximum height of the confined NLC, and Cousins *et al.* present a model to describe the height variation across the width of the confined NLC. The current work is directly compared to the assumptions that Cousins *et al.* take for their semi-droplet, and the equation they use to describe the height variation across a semi-droplet that they assume to be isotropic.

Clearly, the dimensions of the confined NLC semi-droplet in any application will be important and this work considers a significant expansion of the semi-droplet dimension; confinement shapes between 0.5 – 1 in aspect ratio, 6 - 13mm in width, and 6 - 20mm in length, with NLC heights between ~20 - 420 μ m were investigated using polarized light images. This wide-ranging study works towards optimization of these parameters for future use in sensors, considering specifically what dimensions offer high-quality and readily observable director fields. We derive a simple geometric model in which the key parameter is the interface angle at the edge of the confinement region and consider it with respect to the model deduced by Cousins *et al.*(39) which employs the cross-sectional area of the confined NLC. Combining the models allows the cross-sectional area, estimated using NLC semi-droplet volume and assuming a constant cross-sectional area along the confinement length, to be used to predict the semi-droplet interface angle. This itself is powerful with our model as the height variation and maximum height can therefore be predicted.

Geometric Modelling of the Semi-Droplets

A large amount of work on modelling of semi-droplets of NLCs has been undertaken by Cousins *et al.*(39) who presented an in-depth theoretical description of a specific case of general equations described in an earlier paper(41) on confined NLC within a rectangular geometry with a solid aligning surface and open air/NLC interface, assuming the NLC is static and can be treated as 2D. Cousins *et al.*(39) pinned this NLC semi-droplet at the edges, assumed it to be a thin semi-droplet with symmetry about $x = 0$ and allowed for the assumption that the effects of gravity on the semi-droplet were negligible by ensuring that the semi-droplet half-width, d , is much smaller than the capillary length, L_c , i.e., $d \ll L_c = \left(\frac{\gamma}{\rho g}\right)^{\frac{1}{2}}$ (42), where γ is the NLC/air interfacial tension, ρ is the NLC density and g is gravitational acceleration. For their experimental semi-droplet, Cousins *et al.*(39) filled a $2d$

= 1.2mm, and length, L = 60mm confinement area with ~1μL or ~3μL, of the NLC 5CB. Their confinement was formed using a rubbed alignment layer of PVA surrounded by Teflon. They experimentally validated Equation 1 as the height variation at the very edge of their experimental semi-droplet (x = 400 - 600μm), assuming the material was isotropic, static and with a well-defined edge-pinning position,

$$h(x) = \frac{3\varepsilon(d^2-x^2)}{4d} = \frac{3V(d^2-x^2)}{4d^3L} . \quad [1]$$

In Equation 1, h(x) is the height variation across the semi-droplet's x – axis, A is the cross-sectional area, L is the length and V is the NLC volume of the semi-droplets. $\varepsilon = \frac{A}{d^2}$ and it is assumed that $\frac{A}{d^2} \ll 1$, implying the ridge is thin.

The work by Cousins *et al.*(39) is extremely detailed, theoretically describing the confined NLC semi-droplets in relation to important NLC properties such as the elastic energy of the director field, different possible director field orientations, and anchoring strength. However, in this work we seek to present a simple geometric model that describes the height variation across the width of the semi-droplet, with a focus on experimental parameters. Like Cousins *et al.*'s semi-droplet isotropic model (Equation 1), our model does not consider gravity and is static. In addition, in this current work it is expected that $\varepsilon \sim 0.007 - 0.2$, therefore largely matching the assumptions used in Equation 1. The model we present is not liquid crystal-specific, further simplifying the description of the semi-droplet and making it broadly applicable. In this work, d = 3 – 6.5mm which is somewhat greater than the capillary length for the NLC E7, $L_c \sim 1.57\text{mm}$ (calculated using $\gamma = 24.2 \times 10^{-3} \text{Nm}^{-1}$ (8), $\rho = (0.97 - 1) \times 10^3 \text{kgm}^{-3}$ ^{2*} and $g = 9.81 \text{ms}^{-2}$). This contrasts to the assumption in Cousins *et*

² *See Synthon Chemicals Safety Data Sheet for 'Liquid crystal Mixture E7'.

al.(39) where $d \ll L_c$, therefore can be used as a comparison to see where the assumption of negligible gravitational contributions breaks down.

To form our simple geometric model, we assume that the base of the semi-droplets with width $2d$, are chords of a circle and the height is therefore described by the minor arc of the minor segment of a circle with radius r , as shown in Figure 2. Then, Equation 2,

$$h(x) = d \left(\frac{\alpha}{\sin(\theta_1)} - \frac{1}{\tan(\theta_1)} \right), \quad [2]$$

where,

$$\alpha = \left[1 - \left(\frac{x \sin(\theta_1)}{d} \right)^2 \right]^{\frac{1}{2}},$$

describes the variation in height of the semi-droplet, $h(x)$, across the confinement width, x , and can be shown with geometric arguments. We denote the angle that the NLC makes with the surface at the confinement edge as the interface angle, θ_1 , noting that this is not the same as the contact angle of NLC on the polyimide surface since the NLC cannot spread freely due to the confinement shown in Figure 1. To show this, a droplet of E7 was placed onto homogeneous SE130 or silane coated onto glass. On the former, the droplet spread to a very thin layer, whereas on the silane the droplet shape was retained, with a contact angle of $70^\circ \pm 2^\circ$.

FIGURE 2 NEAR HERE

It is assumed in this work that the cross-sectional area of the semi-droplet is constant along the confined length and therefore can be determined from the volume of NLC, known from the dispensing conditions to be between $0.5 - 30\mu\text{L}$, i.e $V = AL$. In such as case it is simple to see in Equation 1 that the NLC maximum height should vary linearly with V . This

is useful as the key experimental parameters in this work are the rectangle's size and the dispense volume of the NLC.

Equating our simple geometric model, Equation 2, with Cousins *et al.*'s(39) isotropic semi-droplet model, Equation 1, at $x = 0$ provides Equation 3,

$$\theta_1 = 2\cot^{-1}\left(\frac{4}{3\varepsilon}\right). \quad [3]$$

This allows for a simple method to predict the interface angle, which itself a powerful tool to predict other properties of the semi-droplet, as Equation 1 describes the semi-droplet height in terms of its cross-sectional area, whereas Equation 2 describes height in terms of θ_1 . The known properties of the NLC semi-droplets as formed are V , d and L , meaning A can be estimated (assuming uniform filling) using $V = AL$. This in turn can be used with d to predict ε with Equation 1, which can then be used with Equation 3 to predict θ_1 . This method to predict θ_1 is necessary as it would be impractical to measure some of the smaller interface angles. When θ_1 is substituted into Equation 2 at $x = 0$, the maximum semi-droplet height is predicted, or with substitution into Equation 2, $h(x)$ can be predicted.

Although it is not discussed in-depth in this current work, the interface angle could alternatively be used with the simple geometric equation given by Equation 4 to predict the radius of the circle shown in Figure 2,

$$r = \frac{d}{\sin(\theta_1)}. \quad [4]$$

Summarizing, the model given by Cousins *et al.*(39) for a thin semi-droplet that is symmetric about $x = 0$, for an isotropic material within a well-defined confinement area is compared to the geometric model derived here (with the same assumptions), which was created as a simpler approach to describe the shape of the semi-droplets. However, unlike in Cousins *et al.* where $d \ll L_c$, in this work $d > L_c$. We experimentally determine the height

across the whole semi-droplet width and consider whether the model breaks down due to the comparable sizes of the half-width and capillary length. Equation 1 can be used in conjunction with Equation 2 to provide a simple route for predicting θ_1 , which is a valuable property to allow many other properties of the semi-droplets to be predicted.

Methods and Materials

Chemical Patterning

FIGURE 3 NEAR HERE

Glass microscope slides were cleaned in an ultrasonic bath in deionised water with Decon-90, followed by separate washes in deionised water and acetone. Planar polyimide SE130 with a pretilt of $\sim 2^\circ$ (Nissan Chemical Industries, Ltd.) was deposited *via* spin-coating, dried, cured and machine rubbed using a velvet roller before Microposit[®] S1813[®] photo resist (Shipley) was deposited *via* spin-coating. Rectangular shapes were then patterned into the photoresist layer *via* contact photolithography, with a bespoke photomask. The patterns were then developed in a Microposit[®] MF[®] CD-26 developer solution (Shipley), and then rinsed in deionised water. UV exposure of the whole sample with no photomask was completed, before being placed in an oven at 100°C for a minimum of 15 minutes. 1H,1H,2H,2H-Perfluorooctyltrichlorosilane 97% (Thermo Scientific) was deposited onto the surface in a desiccator where nitrogen gas was passed over the samples, before being left under vacuum for ~ 1 hr(43, 44). Any remaining photoresist was removed and rinsed using IPA and deionised water.

NLC Deposition

The NLC, E7 (Synthon) was used to fill the confinement areas as follows. A vial containing the NLC was placed alongside the chemically patterned substrate on a hotplate above the nematic-to-isotropic temperature, T_{NI} ($\sim 60^\circ\text{C}$), before the NLC was pipetted using

specifically measured volumes onto the confinement areas of the substrate. The NLC was spread to the confinement edges using directional compressed air or gentle tilting as required, before removing the sample from the heat. The sample was again heated above T_{NI} , held at a constant temperature, and cooled on a hot stage to remove any air bubbles before imaging. The surfaces were used multiple times and between each new dispense of NLC, the ‘old’ NLC was removed from the surface with IPA, before drying with compressed air and/or evaporation on a hotplate.

Imaging

The macroscopic sample areas considered in this work were too large to image using a typical polarizing microscope. Therefore, to image the NLC samples using polarized light, a bespoke imaging system was created to image with a large field of view between $\sim 15 - 94\text{mm}$. The resolution of $9.26 - 27.78\mu\text{m}$ is such that there is little compromise with the quality of the images. The imaging apparatus can be used with no polarizer, one or two polarizers, and in both transmission and reflection modes. This set-up allows images to be recorded under a variety of illumination and polarization conditions. Further fabrication and imaging details can be found in the *supplementary information*.

Measurement of Semi-Droplet Height

The birefringence of the confined NLC could be readily imaged when the rubbing axis of the confinement was held at 45° to the crossed polarisers in the imaging system, as can be seen Figure 4a which shows typical data. To experimentally validate the models presented in the previous section, the height of the semi-droplet was measured across its width and length by observing the number of pink birefringence fringes in the image. These fringes satisfy the full-wave condition of the birefringent NLC for green wavelengths; green is absorbed by the analyser, and pink passes through. This full wave condition can be written in terms of the

height $h = \frac{m\lambda}{\Delta n_{\text{eff}}}$, where $m \in \mathbb{Z}$, the first fringe closest to the droplet edge corresponds to $m = 1$ and a green wavelength of $\lambda = 0.53 \pm 0.04\mu\text{m}$ is assumed.

The effective birefringence of the sample, Δn_{eff} , can be calculated, assuming a hybrid aligned nematic (HAN) director variation within the semi-droplet (Figure 4c), with a small pretilt planar alignment ($\sim 2^\circ$) at the solid substrate, and homeotropic orientation at the NLC/air interface. The HAN director field is a good approximation across the cross-section of the semi-droplets as the semi-droplet heights are approximately three orders of magnitude smaller than the radius of the circle they are modelled (Figure 2), with a small region near $x = \pm d$ where the assumption will break down. The extraordinary and ordinary refractive indices of E7 are taken as $n_e = 1.73$ and $n_o = 1.52$, respectively at approximately 25°C (45), giving $\Delta n_{\text{eff}} = 0.1$ (see the supplementary information for the full calculation). Figure 4a shows a typical sample where a 6mm square confinement size is filled with $V = 0.5\mu\text{L}$ E7 and six birefringent fringes can be seen. Counting from the edge, where the first fringe is $m = 1$, and using $h = \frac{m\lambda}{\Delta n_{\text{eff}}}$, the height profile can be measured, as shown in Figure 4b, in this case with a maximum height of $h = 32 \pm 6\mu\text{m}$.

FIGURE 4 NEAR HERE

A factor to consider when evaluating what contributes to an ‘optimum’ semi-droplet height for sensing is that alignment layers for NLCs are typically only effective up to a layer thickness of $\sim 100\mu\text{m}$ from the anchoring condition. Therefore, for the taller semi-droplets there may be some disorder in the centre of the confined NLC which would make the HAN director field assumed in Figure 4c less accurate in the central regions and therefore have some effect on Δn_{eff} .

Results and Discussion

Semi - Droplet Height

Figure 5 shows polarized light images of samples with varying NLC semi-droplet heights, produced by dispensing different volumes of material into the 6mm square confinement size. Examples of 11mm square, 16 x 13mm rectangular and 20 x 10mm rectangular confinements, also with varying semi-droplet heights are given in Figures 6 and S3.

Figures 5 a–d, Figures 6 a-c,e-g,i-l and Figures S3 a,b,g,h show clear birefringent fringes that allow for measurements of the height across the semi-droplets as described. ϵ , the interface angle and the maximum height can all be predicted from the dispensed volume of NLC and geometric equations, as was described in the section on modelling. Figure 7 compares the experimentally determined height with the predicted height for these semi-droplets, removing geometric effects by scaling the volume of dispensed NLC by the surface area of each confinement size, $(\frac{V}{2dL})$. Figure 7a shows that the heights predicted using the model are in good agreement with the experimental data, i.e. within three uncertainties (Figure 6l), two uncertainties (Figures 5a,c, 6b,i-k) or, as is the case for the majority of the samples, within one uncertainty, across the different confinement dimensions and NLC volumes. It is expected that the data should fall on a straight line with gradient $\frac{3}{2}$ (Equation 1), and this is also shown in the figure. Therefore, we can conclude that our simple model can be used to predict the height of the semi-droplet from the dispense volume reasonably well.

FIGURE 5 NEAR HERE

FIGURE 6 NEAR HERE

Figure 7b shows the fractional difference, Equation 5, between the experimentally measured maximum height of the semi-droplets and those predicted from the models,

$$\text{Fractional difference} = \frac{h_{\text{measured}} - h_{\text{predicted}}}{h_{\text{measured}}}. \quad [5]$$

Considering this fractional difference, despite the good agreement in the height information (Figure 7a), there remain some systematic differences, especially for some of the larger rectangles used, highlighted in Figure 7b, that need to be accounted for.

FIGURE 7 NEAR HERE

One possibility for this discrepancy is that some samples are clearly underfilled (e.g. Figure 5a), and some are overfilled (e.g. Figure 5h) and in such cases, assuming that d and L are accurately known is somewhat questionable. The blue lines on Figures 6i-l for 20 x 10mm confinement sizes show where the size of d and L was measured directly to obtain a more accurate NLC coverage surface area within the rectangle. These four samples were chosen because, as a confinement size group of samples, they have the worst agreement in general between the measured and predicted maximum heights, where Figures 6i-k agree within two uncertainties, and Figure 6l agrees within three uncertainties. Samples 6i-l are marked in Figure 7b. The maximum height was predicted in the same way using the models (i.e. estimating A from $V = AL$, then predicting ϵ , followed by θ_1 and finally height at $x = 0$), but with the measured d and L values, and compared to the fractional difference for the heights assuming known d and L values (Figure 7b). In all cases, using the measured d and L values moves the points for these four samples closer to the fractional difference = 0 dashed line.

A second possible reason for the discrepancies in the measured and predicted heights is that the assumption that the semi-droplet cross-sectional area is a minor segment of a circle is incorrect. Figure 8 directly compares the measured and predicted heights across the semi-droplets for three relatively small heights (measured heights between 32 - 130 μm) for each of

the four confinement dimensions. Equations 1 and 2 are fitted to the measured heights, where the cross-sectional area and interface angle, respectively, are allowed to vary. It can be seen that the models are indistinguishable for this parameter space and that there is an excellent fit for the semi-droplets with the smallest heights, but that the actual shapes of the semi-droplets deviate from the model as the height increases. In particular for the semi-droplet profiles with greater heights, the centres are flatter and there is more curvature at the edges. We suggest that this distortion can be attributed to the effect of gravity as neither model includes gravitational terms, and the height is much smaller than the width in all cases, so it is to be expected that the middle region will be relatively flattened.

FIGURE 8 NEAR HERE

Ensuring that the geometry is smaller than the capillary length allows us to make the assumption that gravitational effects can be neglected; for E7, $L_C \sim 1.57\text{mm}$. In this work $d > L_C$, i.e for the 6mm square confinements, $\frac{d}{L_C} \sim 1.91$; for the 20 x 10mm rectangles, $\frac{d}{L_C} \sim 3.18$; for the 11mm squares, $\frac{d}{L_C} \sim 3.5$, and for the 16 x 13mm rectangles, $\frac{d}{L_C} \sim 4.14$, i.e. we have relaxed this important constraint in the expectation that the semi-droplets will be more readily visible without the need for a microscope. We find qualitatively that for heights $\lesssim 50\mu\text{m}$, the fits of the models to the data in Figure 8 are in good agreement, regardless of the ratio of the semi-droplet half-width to the capillary length.

Figure 9, like Figure 8, compares the measured and predicted heights of the semi-droplets, however along their lengths (y-axis). A common feature in the measured heights for Figures 8 and 9 is their asymmetry, as shown relative to the dashed line at $x = 0$. As no special effort was made to ensure the stage of the imaging system was perfectly flat, there was probably a tilt of a few degrees in the x- and y- axes, which would explain this asymmetry due to gravity, but does not have a significant or adverse effect on the semi-

droplets. When the semi-droplets are imaged, they are in a steady state. The asymmetry is most clearly seen both along the width and length for a measured height = $101\mu\text{m}$ for the 20 x 10mm samples (Figure 8,9d, with the polarized light image in Figure 6l). Along the length for the rectangles, there is a clear increase of asymmetry for the rectangles as compared to the squares, with the 6mm square generally the most symmetric. It is to be expected that a more asymmetric shape of the NLC is possible in the lower aspect ratio rectangles; the squares have an aspect ratio of 1, whereas the rectangles have aspect ratios of approximately 0.8 for the 16 x 13mm and 0.5 for the 20 x 10mm rectangles. It is also to be expected that the shape is less symmetric along the length of the rectangular samples, especially in the longest samples (20 x 10mm), as the increased length will allow for gravity to have a larger effect on the symmetry of the semi-droplet.

FIGURE 9 NEAR HERE

The solid black lines at the edge of the plots indicate the expected values for $x = \pm d$ (Figure 8) or $y = \pm \frac{L}{2}$ (Figure 9) and allow us to consider the quality of filling of the semi-droplet within the confinements. All the samples presented in Figure 8 demonstrate a good agreement with these lines, except for the those with measured heights = $130\mu\text{m}$ for the 11mm square confinement, and measured height = $74\mu\text{m}$ for the 16 x 13mm rectangle confinement (Figures 8b,d, with the polarized light images in Figures 6c,j, respectively). In the x – axis, they are overfilled by $0.15 \pm 0.08\text{mm}$ and $0.2 \pm 0.1\text{mm}$, respectively, hence there are only in slight differences with the measured and expected sample edge, indicating that there is overall good filling along the width of the confinement. For Figure 9, the 20 x 10mm size confinements (Figure 9d) are the only examples given with significant under- or overfilling. For Figure 6i (measured height = $48\mu\text{m}$) this corresponds to an underfill at the top of the confinement (positive x-axis in Figure 9) of $1.2 \pm 0.1\text{mm}$; for Figure 6j (measured

height = $74\mu\text{m}$), there is an overfill at the bottom of the confinement (negative x-axis in Figure 9) of $0.8 \pm 0.1\text{mm}$, and an underfill at the top of $1.1 \pm 0.1\text{mm}$, and for Figure 6l (measured height = $101\mu\text{m}$) the overfill at the bottom is $0.4 \pm 0.2\text{mm}$ and the underfill at the top is $2.0 \pm 0.2\text{mm}$. Therefore, this size can be ruled out as a choice for useful sensing devices in the future. In general, for the other confinement sizes (Figures 9a-c) however, there is good filling along the length.

Defect Formation in NLC Semi-Droplets

A key consideration of use of this system as a sensor is how clear and reproducible the director fields are before addition of the analyte. A common feature of NLC confined on a stripe surface seen in the literature is a central disclination line. For example, in Bao *et al.*(38), a central disclination is described by an ‘escaped radial’ director field, characterised by alternating defects of strength of ± 1 . Cousins *et al.*(39) describe the central disclination line observed in their work in terms of a discontinuous angle of the NLC director. A similar feature is seen in each of the polarized light images in Figures 5, 6 and S3, i.e. a disclination line, or line of defects that runs approximately perpendicular to the rubbing direction. This is most consistent in the 6mm square and is straightest in the $V = 7\mu\text{L}$ (predicted height = $290\mu\text{m}$, Figure 5f) sample, although samples such as $V = 5\mu\text{L}$ in a 6mm square (predicted height = $208\mu\text{m}$, Figure 5e) have a similar level of quality.

As already discussed, the square confinement shapes (Figures 9a,b) have a generally more symmetric filling than the rectangles (Figures 9c,d). Examples from Figures 5, 6 and S3 demonstrate however that there is a balance to be found for the NLC dispense volume so as not to overfill (e.g. Figure 5h) or underfill (e.g. Figure 5a) the samples. Significant overfilling could impact the quality of the director field significantly, for example in Figure 6d (with a predicted height = $370\mu\text{m}$) has extra domains other than the central disclination line. As the

6mm square confinement was identified as having the straightest central disclination line in general, it should be the focus for identifying the correct volume of the semi-droplet. i.e., qualitatively between $V = 3-5\mu\text{L}$ corresponding to predicted heights = 125 - 208 μm (Figure 5d-e) offer a uniform fill, including to the corners of the confinement, but without overflowing it, suggesting a good choice of parameter space to continue development for sensors.

These key points, i.e. how straight the central defect is, as well as the quality and symmetry of the filling implies that the 6mm square with $V \sim 3-7\mu\text{L}$ is the most suitable for future sensor development. There are clear benefits to this finding, in that less liquid crystal will need to be used to fill the sample than would be needed in a larger confinement size or a higher dispense volume, however a balance must be found between usage of material and sensitivity of the sample. For example, whilst Bao *et al.*(38) present a sample with a straighter central disclination line, the width of their stripes was of the order of μm instead of mm as in this work, hence may well be less sensitive to gaseous stimuli and would have to be viewed using a microscope.

The polarized light images in Figures 5, 6 and S3 suggest that the chemically patterned surfaces used are reusable and reproducible, as a maximum of two different surfaces for each confinement size were used to collect the data and were washed off with IPA in-between refilling with NLC to form the semi-droplets and imaging. There is no significant variation in the director field or quality seen in the polarized light images other than those discussed in relation to the volume dispensed and confinement dimensions, therefore this system could lead to more sustainable future sensing methods, as well as make for safer usage due to IPA being a relatively safe and cheap solvent.

Interface Angle

TABLE 1 NEAR HERE

As was mentioned earlier, the interface angle is a powerful parameter as it can allow many other semi-droplet parameters to be predicted including maximum height and height variation along the semi-droplet width (Equation 2), the radius of the circle on which the semi-droplets are modelled (Figure 2, Equation 4). In the results and discussion sections, it was determined that the 6mm squares have the best potential for future work on sensing devices. Therefore, the 6 x 6mm square confinements for $V = 0.5 - 1.8\mu\text{L}$ (Figures 5a-c) are used to investigate the validity of the interface angles predicted from the models, as given in Table 1b (i.e. using $V = AL$ to deduce the cross-sectional area, followed by Equation 1 to predict ϵ , and Equation 3 to predict θ_1). Measurements of the interface angle, Table 1c, were made by applying a linear fit to the first few data points on the left of Figure 8a. All the interface angles presented in Table 1b,c are $< 4^\circ$ which highlights one aspect of why the models presented simplify the prediction of the interface angle and hence the prediction of the height variation across the semi-droplet. i.e., this angle would be difficult to measure directly accurately using contact angle apparatus.

The measured interface angle (Table 1d) is always greater than the predicted interface angle (Table 1c), as would be expected from examination of the experimental data and models in Figure 8a. There are two contributions to this observation. Firstly, the predicted value of θ_1 , having only the uncertainties in V , d and L which are small, is likely to be quite accurate, whereas the measurement relies only on a few data points, and the linear fit is only an approximation of the shape. To determine whether the interface angle deduced from measurement or the model is better at predicting the semi-droplet height, Table 1 also compares calculations (d and e , respectively) with measurements (f). For the $V = 0.5\mu\text{L}$ sample, the predicted height from the measured interface angle is significantly closer to the measured height than the predicted height from the predicted interface angle. However, the

inverse is seen for the $V = 1\mu\text{L}$ and $1.8\mu\text{L}$ samples, though neither agrees particularly well in the case of the larger volume.

The radius of the circle used to model the semi-droplets (Figure 2) can be calculated using the predicted interface angle with Equation 4 and is shown in Table 1g. The fact that the radius is approximately three orders of magnitude larger than the heights further validates the use of the HAN director field (Figure 4c) that was assumed in this work to describe the director along the NLC semi-droplet height.

Conclusions

NLC-based chemical sensing is a growing research area. Here, a novel chemical patterning method has been used to create rectangles with accurately known dimensions on a surface to confine NLC, forming relatively large NLC semi-droplets. These all have a well-defined hybrid alignment due to one rubbed planar surface (solid substrate) and one homeotropic surface (NLC/air). The fabricated rectangles cover a wide dimensional range with widths between 6 - 13mm; lengths between 6 - 20mm, and aspect ratios between 0.5 - 1. The confined NLC semi-droplets had a range of heights between $\sim 20 - 420\mu\text{m}$. This work has therefore investigated a significant range of variables, allowing a better understanding of the limiting factors in the parameter spaces in context of a future sensing device. The lack of a significant change in quality in the polarized light images noted when reusing the confinement surfaces *via* washing with IPA in-between imaging and refilling with NLC, suggests that the surfaces are reusable which is beneficial for a potential rapid, multi-use sensor system.

A simple model to describe the height of the NLC across the stripe was derived and compared to an existing, more detailed model. The two models had a similar experimental and theoretical geometry, however the model in this work is calculated using the interface

angle, while the existing model utilizes the cross-sectional area. Therefore, a combination of the two models allows for the cross-sectional area (estimated using the volume of the semi-droplet and assuming that the cross-sectional area is constant along its length) to give a prediction of the interface angle. This in turn can be used to predict the height variation across the semi-droplet, as well as the maximum height. These predictions were found to be in excellent agreement with experimentally measured semi-droplet heights, found from the birefringent fringes of the NLC polarized light images, lending validation to the model. The height variation was deduced across the whole semi-droplet width, whereas Cousins *et al.*(39) evaluated this at the semi-droplet edge. Systematic differences such as the effect of under- or over-filling the confinements and the potential effect of gravity were discussed. It was shown that the height of the NLC in semi-droplets is both more symmetric in the width- rather than length- direction, and that the squares, particularly the 6mm square, were most symmetric. The model was found to agree well with measurements for heights $\lesssim 50\mu\text{m}$, even though the dimensions exceeded the capillary length of the NLC, $\frac{d}{L_c} > 1$, irrespective of the value of the ratio $\frac{d}{L_c} \sim 1.91 - 4.14$.

The 6mm square was seen to exhibit a more well-defined, straight, and central defect line (a feature commonly seen in NLC semi-droplets) than the 11mm square or rectangular confinements. The study has also shown that there must be enough NLC to fill the sample, but not so much to overfill it or to cause a decrease in the quality of the director field by causing extra domains to form in the semi-droplet. Of the samples investigated, the $V \sim 2 - 7\mu\text{L}$ -filled 6mm squares, with predicted heights between $\sim 125 - 290\mu\text{m}$ demonstrated the best director field of those presented for simplicity and reproducibility as a sensor. Combined with the good symmetry as previously discussed, the 6mm square is suggested to be a good parameter space for future sensing work.

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Declaration of Interest

No known conflicts of interest.

Data

The data associated with this paper can be found in DOI: <https://doi.org/10.5518/1606>

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MAIN TEXT TABLE

(a)	(b)	(c)	(d)	(e)	(f)	(g)
NLC Volume, $V/\mu\text{L}$	Predicted (Model) $\theta_1/^\circ$	Measured (Linear fit) $\theta_1/^\circ$	Height from predicted θ_1 (b) $/\mu\text{m}$	Height from measured θ_1 (c) $/\mu\text{m}$	Measured height, $h/\mu\text{m}$	Predicted radius, r , from θ_1 (1b)/mm
0.5 ± 0.01	0.80 ± 0.03	1.32 ± 0.06	21 ± 1	35 ± 2	32 ± 6	220 ± 10
1 ± 0.01	1.59 ± 0.07	2.3 ± 0.1	42 ± 2	60 ± 3	42 ± 6	108 ± 5
1.8 ± 0.01	2.9 ± 0.1	3.7 ± 0.2	75 ± 3	98 ± 5	58 ± 7	60 ± 3

Table 1 : Parameters determined from measurements or predictions for (a) three NLC volumes of 6 x6mm squares. (b) The predicted interface angle from calculating $V = AL$, estimating ε (Equation 1), and finally Equation 3. (c) The interface angle measured from linear fits of the first few data points on the left-hand side of the height variation plots in Figure 8a. (d) The measured heights in the polarized light images (Figures 5a-c) (e) The heights predicted using Equation 2 from the θ_1 in (b). The heights predicted using Equation 2 from the θ_1 in (c). (g) The radius of the circle on which the simple geometric model is based (Figure 2).

MAIN TEXT FIGURES

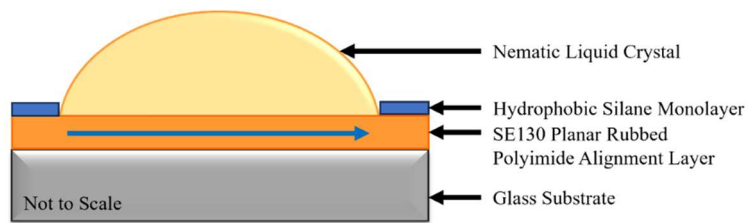


Figure 1- Schematic side-view of confined NLC semi-droplet in chemically patterned rectangles. The NLC is confined between hydrophobic monolayer regions and sits on a planar rubbed polyimide alignment layer. The blue arrow represents the rubbing direction of the alignment layer. The schematic is not to scale.

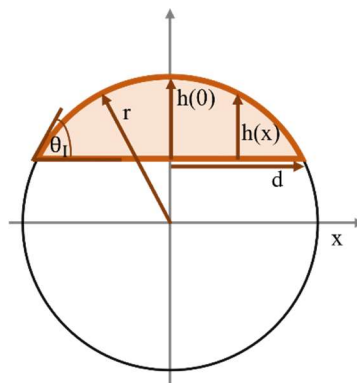


Figure 2: Diagram of the geometric model parameters used to describe the cross-section of an NLC 'semi-droplet' confined in a rectangular geometry showing the maximum height, $h(0)$; variation of height with x , $h(x)$; half-width of the stripe, d ; radius of the circle from which the confined NLC shape is formed, r , and interface angle, θ_1 . The distance $2d$ is the length of the minor chord of the circle and the shaded area is the cross-sectional area of the semi-droplet, A . The height of the semi-droplets in this work are of the order of 10-500 of μm , and the radius of the circle is of the order of 10-100 of mm .

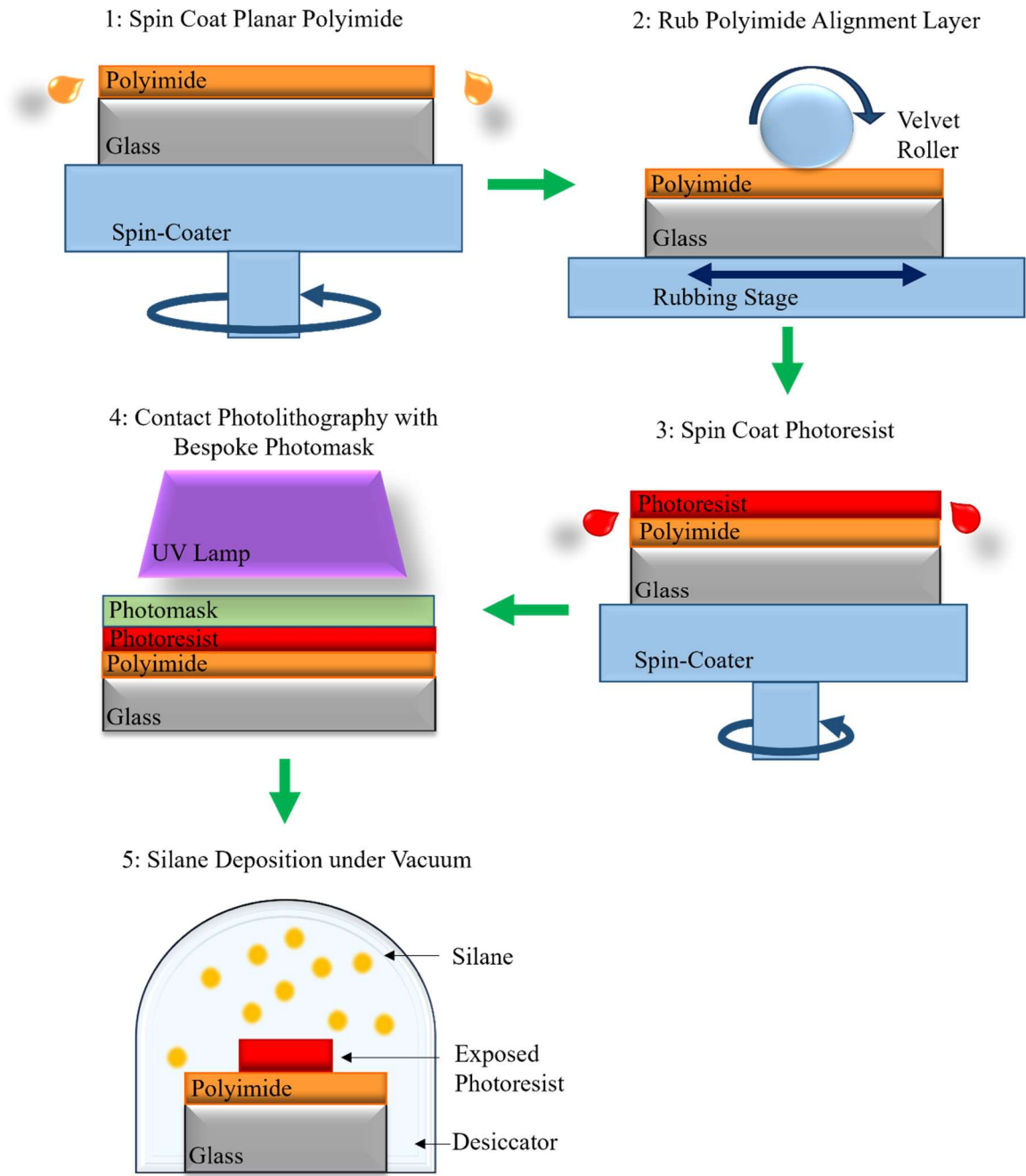


Figure 3- Key steps in the fabrication of the chemically patterned glass for NLC confinement in rectangles to form 'semi-droplets'. The schematics are not to scale.

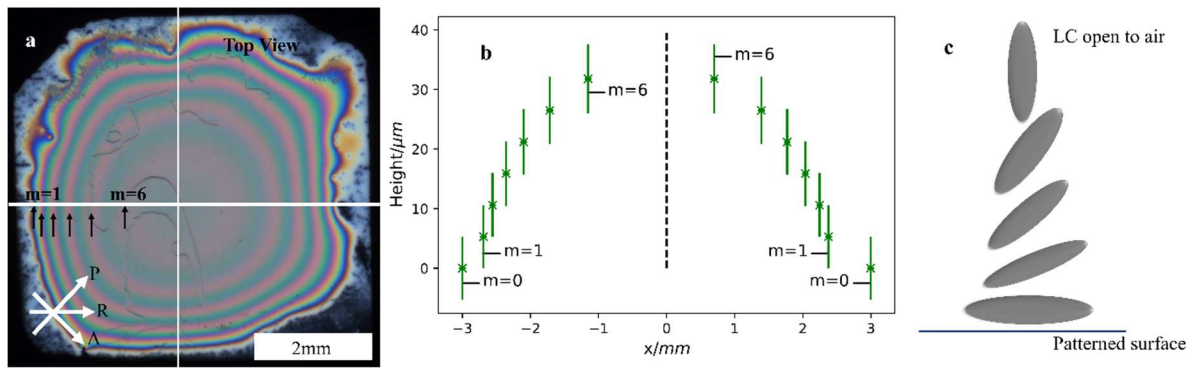


Figure 4: (a) Top view polarized light image of 0.5 μ L NLC confined in 6mm square chemically patterned surface with top surface open to air. The value of m represents the number of pink birefringent fringes, counting from the semi-droplet edge. P, A and R show the relative directions of the polarizer, analyser and rubbing, respectively. White lines show the cross-section along which the centre-to-centre distances of the fringes have been measured to deduce the height variations. The scale bar is 2mm. (b) Plot of the centre-to-centre distances of the pink birefringent fringes along the width marked by a white line in (b), with their corresponding measured heights. (c) Hybrid-aligned nematic section which is used to estimate the effective birefringence of the NLC semi-droplets confined within rectangles. The pretilt at the solid substrate/NLC interface is assumed to be 2° and homeotropic alignment is assumed at the NLC/air interface.

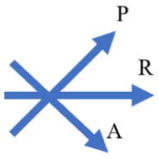
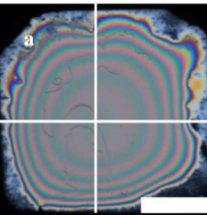
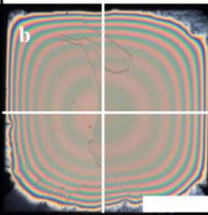
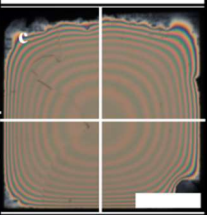
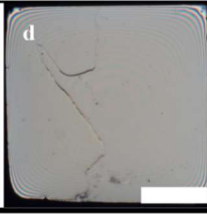
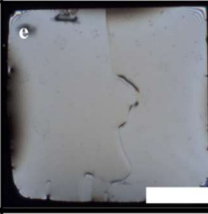
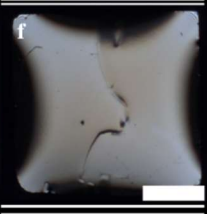
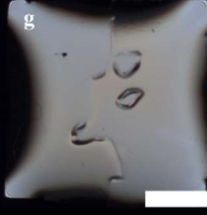


NLC Volume, V/μL	0.5 \pm 0.01	1 \pm 0.01	1.8 \pm 0.01
Measured height, h/μm	32 \pm 6	42 \pm 6	58 \pm 7
Predicted height, h/μm	21 \pm 1	42 \pm 2	75 \pm 3
			
NLC Volume, V/μL	3 \pm 0.01	5 \pm 0.01	7 \pm 0.01
Measured height, h/μm	110 \pm 10	-	-
Predicted height, h/μm	125 \pm 6	208 \pm 9	290 \pm 10
			
NLC Volume, V/μL	8 \pm 0.01	9 \pm 0.01	10 \pm 0.01
Measured height, h/μm	-	-	-
Predicted height, h/μm	330 \pm 10	380 \pm 20	420 \pm 20
			

Figure 5: Polarized light imaging of varying NLC ‘semi-droplet’ volumes confined in 6mm squares on chemically patterned surfaces with a rubbed alignment layer on a solid substrate and an NLC/air interface. Maximum heights measured using pink birefringent fringes are compared to those predicted from calculation of the semi-droplet cross-sectional area ($V = AL$), leading to predictions of ϵ (Equation. 1), interface angle (Equation. 3) and finally, height (Equation 2). White lines show the cross-sections along which the centre-to-centre distances of the fringes have been measured to deduce the height variations across the semi-droplet width and length. The rubbing direction is at 45° to the crossed polarisers, with arrows marked P, A and R to show the relative directions of the polarizer, analyser and rubbing respectively. The scale bars are 2mm. The cropping of the images was varied to

ensure that the field of view required to capture all the information (e.g. any overflowing liquid crystal) to be retained while maximising the image visibility.

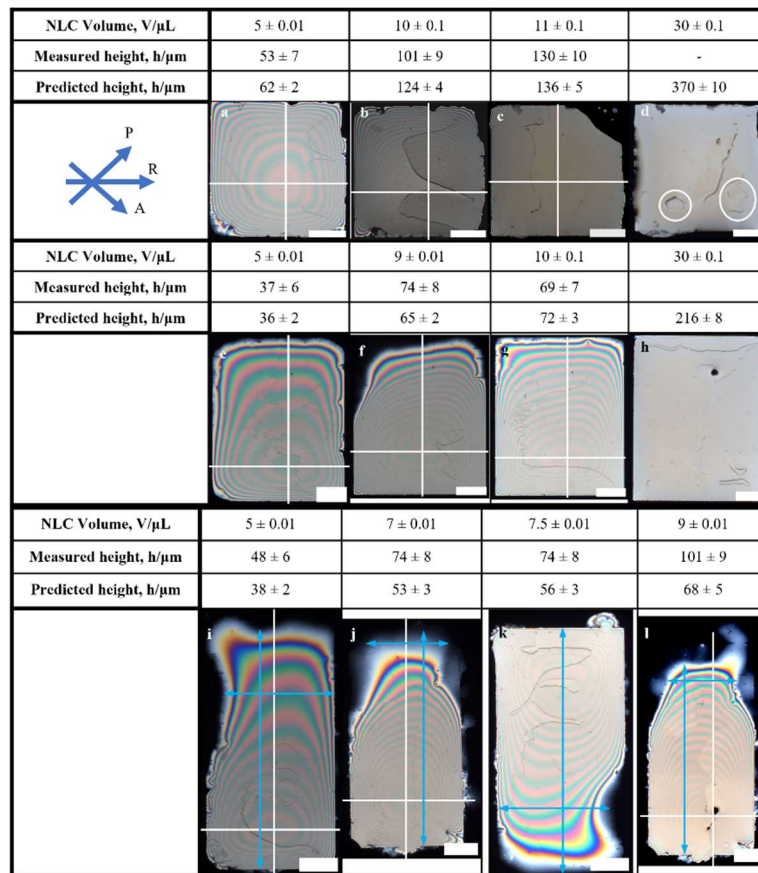


Figure 6: Polarized light images of varying NLC ‘semi-droplet’ volumes confined in rectangles on chemically of varying dimensions: (a-d) 11 x 11mm; (e-h) 16 x 13mm; (i-l) 20 x 10mm, on patterned surfaces with a rubbed alignment layer on a solid substrate and a NLC/air interface. Maximum heights measured using pink birefringent fringes are compared to those predicted from calculation of the semi-droplet cross-sectional area ($V = AL$), leading to predictions of ε (Equation. 1), interface angle (Equation. 3) and finally, height (Equation 2). White lines show the cross-sections along which the centre-to-centre distances of the fringes have been measured to deduce the height variation across the semi-droplet width and length. Blue lines show the width and length measured to approximate the true surface area of NLC. The rubbing direction is at 45° to the crossed polarisers, with arrows marked P, A

and R to show the relative directions of the polarizer, analyser and rubbing respectively. The scale bars are 3mm. Extra domains other are sometimes seen when the confinement is overfilled, as circled in (d) as an example. The cropping of the images was varied to ensure that the field of view required to capture all the information (e.g. any overflowing liquid crystal) to be retained while maximising the image visibility.

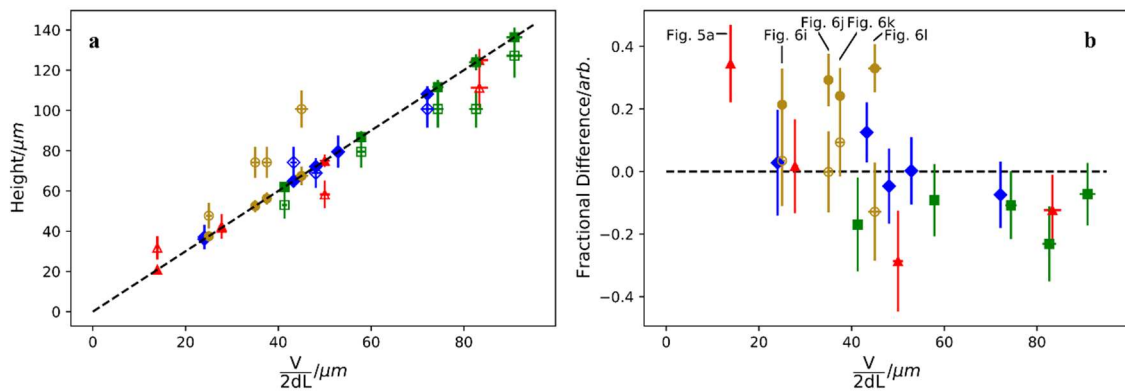


Figure 7: Comparison of measured and predicted maximum heights for four different confinement dimensions: 6 x 6mm (red triangles), 11 x 11mm (green squares), 16 x 13mm (blue diamonds), 20 x 10mm (gold circles). (a) . Maximum height predicted from the models (closed data points), vs. the height measured using the number of birefringent fringes (open data points). A black line of the expected $y = \frac{3}{2}x$ (Equation 1) is added to further validate the models. (b) Fractional difference between the measured and predicted maximum heights assuming no deviation from the expected d and L values (closed data points). For a selection of samples with less good agreement between the measured and predicted heights, heights are calculated using the same models, but with a measured d and l to reflect the true NLC area (open data points). The corresponding polarized light images where this comparison is completed are marked on the figure. $\frac{V}{2dL}$ is calculated using the known d and L , allowing for a clear comparison. A dashed line is added at $y = 0$ for ease of analysis.

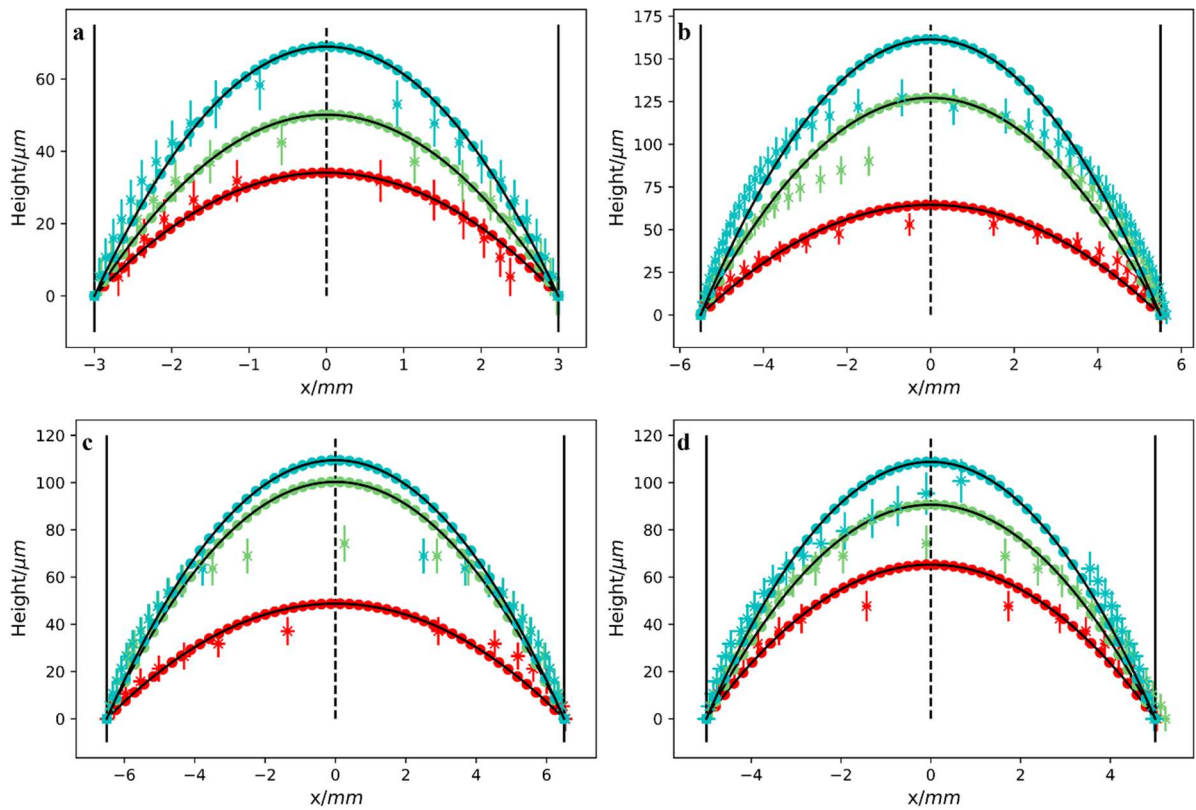


Figure 8: Height variation using the centre-to-centre distances of pink birefringent fringes across NLC semi-droplet widths for three NLC dispense volumes, V , and four confinement sizes: (a) 6 x 6 mm with $V = 0.5\mu\text{L}$ (red), $1\mu\text{L}$ (green), $1.8\mu\text{L}$ (blue). (b) 11 x 11 mm with $V = 5\mu\text{L}$ (red), $10\mu\text{L}$ (green), $11\mu\text{L}$ (blue). (c) 16 x 13 mm with $V = 5\mu\text{L}$ (red), $9\mu\text{L}$ (green), $10\mu\text{L}$ (blue). (d) 20 x 10 mm with $V = 5\mu\text{L}$ (red), $7\mu\text{L}$ (green), $9\mu\text{L}$ (blue). The data is fitted to both Equation 2 (black line), or Equation 1 (circles). A dashed line is included at $x = 0$, as well as solid lines at the expected edges of the confinement shapes.

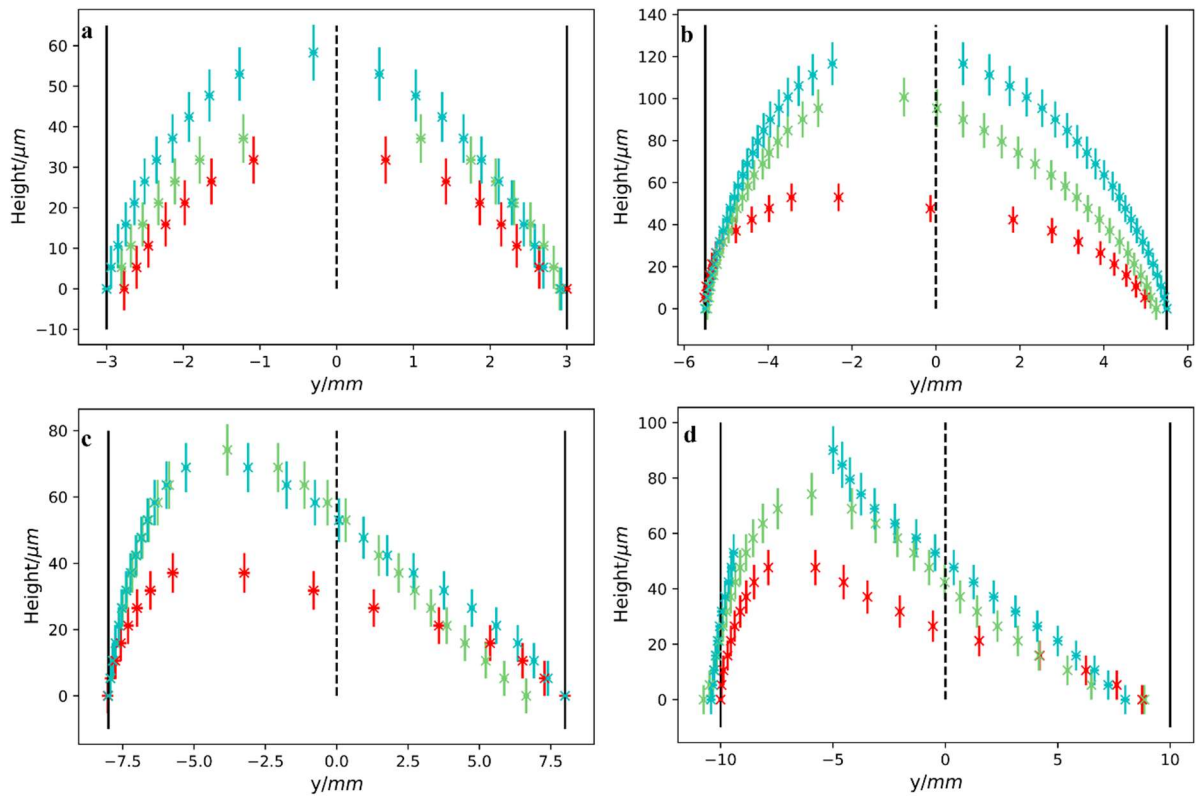


Figure 9: Height variation using the centre-to-centre distances of the pink birefringent fringes across NLC semi-droplet lengths for three NLC dispense volumes, V , and four confinement sizes: a) $6 \times 6\text{mm}$ with $V = 0.5\mu\text{L}$ (red), $1\mu\text{L}$ (green), $1.8\mu\text{L}$ (blue). (b) $11 \times 11\text{mm}$ with $V = 5\mu\text{L}$ (red), $10\mu\text{L}$ (green), $11\mu\text{L}$ (blue). (c) $16 \times 13\text{mm}$ with $V = 5\mu\text{L}$ (red), $9\mu\text{L}$ (green), $10\mu\text{L}$ (blue). (d) $20 \times 10\text{mm}$ with $V = 5\mu\text{L}$ (red), $7\mu\text{L}$ (green), $9\mu\text{L}$ (blue).