1D roughness driven depinning of breath figures on PDMS

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Abstract

Breath figures are typically honeycomb patterns, when formed over smooth surfaces. However, in the presence of underlying constraints, a dual pattern - one over the form of constraint and the other as if on smooth surfaces - are seen. In the present study, the formation of a larger, deformed hexagon-like structure with internal honeycombs is reported in the case of aqueous breath figures formed on PDMS polymer coated over the grooved side of a DVD. The results are compared with the breath figures formed over the smooth, unconstrained side of DVD as a substrate and also with ethanol as environment in place of water. The distortion of the hexagonal pattern is attributed to depinning of the three-phase contact line when the underlying 1D constraints are of the order of 1A.

1 Introduction

Water vapour condensing on cold surfaces self-assemble to form patterns called breath figures. [1]. Energetics demand that the structure of the thus formed droplet pattern (on any surface) be that of a honey-comb [2]. This idea can be extended to include polymers since soft-surfaces will “yield” to the drop placed over it. If a polymer solution in a volatile solvent is placed in a humid atmosphere, there is an evaporative cooling which leads to self-assembled array of condensed water droplets. The solvent and water evaporate, leaving behind patterned pores [3]. The detailed mechanism of formation of breath figures is well-known [4, 5]. They can form not only on solid surfaces
but also on liquids surfaces [6]. Three interfaces, namely that between the solution and the substrate, the solution and water droplets, and the film surface and air play important roles in determining both the structures of the patterned films [3].

An uniform 2D surface with no constraints underneath yields a honeycomb structure of self assembled droplets. If the underlying surface (called the substrate) has additional constraints such as bumps and lines, they are reflected in the breath figure pattern formed. The underlying constraint in the case of polymer patterning comes from the surface over which the polymer layer is coated.

Constraints on the underlying substrate have been introduced previously by depositing the polymer such as PDMS (without block copolymerization) over a TEM grid or a grating [7, 8]. The underlying asymmetry of the grid/grating causes the polymer surface to undulate, which in turn alters the breath figure formed on the surface. A representative diagram for patterns formed on TEM grid and parallel grating are shown in Figure 1.

![Figure 1: Patterns formed inside and over the TEM grid and parallel grating](image)

The presence of a 2D constraints when polymer is deposited over a TEM grid yielded a double pattern of the breath figures deposited. Honeycomb structures were formed at a separation of 50 Å. These correspond to the underlying TEM grid lines of the same dimension. The intermediate space is filled with a second honeycomb structure of a smaller dimension [8].

1D constraints have been introduced by the use of optical gratings of separation 50μm. A similar pattern was seen with the difference that in the case of TEM grid, the outer structure is that of a square while in the case of grating the outer structure is that of straight lines [7].

In the present paper we discuss the effect of 1D constraints on the honeycomb pattern formed by water/ethanol on polymer coated over the grooved surface of a DVD (digital versatile disk). We find that the presence of 1D constraints of the order of 1Å lead to a depinning of the contact line, as sug-
gested by de Gennes \[9\] and hence to the formation of a double honeycomb structure with one corresponding to the subsequent pinning of the depinned contact line and the other to the area in-between the depinned lines.

2 Theory

When a liquid droplet is placed on a solid surface, it can completely spread over the surface, partially spread or not spread at all. This phenomenon is called wetting and the affinity of a solid surface to be wetted by a liquid is called wettability. Wettability of a solid surface is quantified in terms of contact angle which is the angle formed between the tangent to liquid-vapor interface and the tangent to the solid-liquid interface at the three phase contact line. The thermodynamic equilibrium condition for a solid-liquid-vapour system is given by

$$\cos \theta_Y = \gamma_{SV} - \gamma_{SL} / \gamma_{LV} \quad (1)$$

where $\gamma_{ab}$ are the inter-facial tensions associated to each interface [SV,LV and SL] and $\theta_Y$ is the Young's contact angle\[10\]. This condition is called Young's equation (Figure 2)

\[\text{Figure 2: Three phase contact line- -Young's equation}\]

The triple line/three phase contact line defined as a set of points that are in contact with the solid, liquid and vapor phases plays an important role in governing wettability of a surface and is shown in Figure 3. Contact angle is determined by the chemical heterogeneities, surface topology and also the ability of a contact line to remain pinned at the defects \[11\]. Hence the contact angle on the smooth surface is not the same as on the rough surface. For a non-ideal surface, apart from the equilibrium contact angle, there are other
two angles called advancing contact angle and receding contact angle. Advancing contact angle is the maximum static contact angle and the receding contact angle is the minimum static contact angle that the surface can have. The contact angle for a real surface takes on a range of values between these two extremes, i.e., the advancing and receding contact angle. The difference between these two contact angles is called contact angle hysteresis \([12]\) i.e.,

$$\theta_{\text{adv}} - \theta_{\text{rec}} = \theta_H \quad (2)$$

And this is related to surface tension and geometrical factor as

$$\theta_{\text{adv}} - \theta_{\text{rec}} = \left(\frac{8U}{\gamma R_0}\right)^{1/2} h(\theta) \quad (3)$$

where \(R_0\) is the initial radius of the droplet, \(U\) is the potential barrier to be overcome by the droplet under its displacement, \(\gamma\) is the surface tension and \(h(\theta)\) is the geometrical factor of the hysteresis.

The liquid droplet in contact with a rough surface can adopt any one of the following three wetting configurations namely the Wenzel, Cassie-Baxter or the Cassie impregnating wetting state. In the Wenzel state the liquid is in conformal contact with all the topological features of a rough surface \([13]\). The effective contact area between the droplet and the surface is given by Wenzel’s expression:

$$\cos \theta_W = r \left\{ \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \right\} = r \cos \theta_Y \quad (4)$$

where, \(\theta_W\) and \(\theta_Y\) are Wenzel’s and Young’s contact angles and \(r\) is Wenzel’s roughness factor is defined as the ratio of the actual area of a rough surface to the geometric projected area.

In the Cassie-Baxter state \([14]\), the air is trapped in between the solid and
the liquid and the apparent contact angle in this state is calculated using the expression,

$$\cos \theta_s = -(1 - f_s) + f_s \cos \theta_Y$$

where $f_s$ is the fraction of the surface in contact with the liquid. The figures showing Wenzel and Cassie-Baxter state are shown in Figures 4 and 5.

Breath figures formation involves the self assembly of water droplets formed by the condensation of water vapour on a surface. Condensation is usually caused by the difference in temperature between the atmosphere and the surface, the later being cooler. In the case of surfaces coated with polymer solution, the cooling is a consequence of evaporation of the solvent. Once the solvent is completely evaporated, the temperature of the surface rises again to ambient temperature. Then water droplets evaporate, leaving behind an array of pores.

The formation of breath figures undergoes different stages. In the first stage, the droplet nucleate on the substrate surface. In this stage surface coverage by droplets is low. Droplet diameter grows with time as $d \propto k t^{1/3}$, where
k is the function of airflow velocity and temperature. In the second stage the droplets grow until they touch each other [15]. In this stage the surface coverage is maximum and droplets interact closely together. The entropy of the system decreases due to the rearrangement of droplets in close-packed honeycomb fashion. For the same reason, the number of drops with six other neighboring droplets (typical of honeycomb structures) increases. As a result of these stages, a roughly monodisperse distribution of droplets is obtained. This is because, the space released by droplet merging is insufficient for the new nucleation to occur. As time increases coalescence dominates. This favors renucleation of droplets creating enough spaces to occupy droplets. In this phase, droplets diameter grows as \( d \propto t \) [15].

![Figure 6: Stages of breath figure formation](image)

In the absence of coalescence, the formation of ordered honey comb pattern is favored. Marangoni convection, an effect caused by gradient of surface tension at the interface between two phases (liquid and vapor) and the formation of layer of polymer around the water droplet due instant precipitation favors non-coalescence of droplets [2]. The long range order of these droplets is then driven by the long range attractive and repulsive forces. This leads to a surface filled with water droplets stabilized by solvated polymer layer. The various stages of breath figure formation is shown in Figure [6]

The early stages of droplet spreading can be explained with the depinning and pinning events at the contact line. For a smooth surface, the movement of contact line is negligible. For a surface having chemical heterogeneities or
geometrical asperities, the behaviour of partially wetting droplets is complicated by the movement of solid-liquid-gas contact line.

For a surface with parallel grooves, the contact line is either parallel to the grooves and it is pinned on the grooves or the contact line lies at an angle to the grooves and the contact line can be displaced continuously without any pinning. This holds only when the grooves are infinitely long and close to each other like that of number grooves in the case of capillaries normal to the axis [9].

When the contact line moves over the solid surface there are often points that remain pinned, prompting the contact line to suddenly jump to a new position [10]. The pinning is a consequence of opposition that a surface presents to the movement of liquid front. On pinning, the droplets evaporates. Droplets on a surface have two different modes of evaporation: constant contact angle mode and constant contact radius mode. In the former mode, during evaporation, the contact angle is reduced initially having fixed contact radius as the contact line is pinned. When this reducing contact angle reaches receding contact angle, the contact radius starts varying, maintaining a constant contact angle. In this mode, the volume of the droplet varies with respect to time, while in constant contact radius mode, the droplet is pinned and the rate of change of volume of the droplet is constant [17].

3 Experimental Techniques

A piece of commercially available SONY recordable DVD was used as substrate in the present study. Both the grooved and ungrooved sides of the disc were used for patterning for the sake of comparison. Polydimethyl siloxane (PDMS) from SIGMA Aldrich and chloroform (purity 99.9%) purchased from EMPLURA were used as polymer and solvent respectively.

The disc was cut into a piece of 1 cm × 1 cm. The aluminium layer was peeled off from the surface using the forceps. The side facing aluminium layer was grooved and the other side was smooth surface. Both sides of the surface are made of polycarbonate [18].

Polymer solution was prepared by adding 0.5 ml of PDMS to 10 ml of chloroform. A drop of about 300 microliter of this solution was cast over the grooved/ungrooved sides of the DVD. In this study PDMS is used without any curing agent since there is no lift-off process involved. A petri dish is filled with 2ml of distilled water. A stand for the substrate is placed in the dish containing water at a height of 3mm. The substrates coated with PDMS
were placed over the stand. The entire experimental setup as covered with a glass jar to avoid interaction with atmosphere.

The solvent was allowed to evaporate under humid atmosphere by passing moist air towards the sample by means of a air flow pump. Since high relative humidity favours better pattern formation relative humidity of 78 % and temperature of 28 degrees were maintained inside the chamber. The humidity and temperature were measured using temperature hygrometer to an accuracy of 1% and 0.1 degree respectively.

![Figure 7: Apparatus setup for breath figure formation](image)

The solvent was allowed to evaporate completely under this humid atmosphere. After complete evaporation of the solvent, the substrates were examined for pattern formation. The same experiment was repeated in non-aqueous environment, ie., instead of water ethanol was filled in the petri-dish. The apparatus set up for breath figure formation is shown in Figure 7.

The formation of pattern was confirmed through confocal microscopy using a Leica TCS SP8 model. Contact angles were measured using Rame Hart contact angle goniometer(model no. 250 with drop image advanced version 2.4) by slowly depositing droplets of 3 microlitre volume of distilled water on the substrate using a micro syringe. Several measurements were taken at different positions of the substrate and all are reproducible upto ± 2°. The advancing and receding contact angles were measured by adding and removing the water from the droplets using automated dispensing system.
4 Results and Discussion

The confocal images are taken for the patterned surfaces. Breath figures on the smooth surface show honey comb pattern with the pore diameter of around $2.5\mu m$. The pores of the honey comb pattern are fairly uniform in size which confirms the unimodal distribution of droplets and also confirms the absence of coalescence of droplets. The honey comb patterns formed on the smooth surface are driven by Marangoni convection and the presence of lubricating polymer film from instant precipitation of polymer. The grooved surface shows an interesting pattern consists of hexagonal like rings of larger droplets and cluster of smaller droplets inside the ring in both aqueous and ethanol environment. The confocal images of both smooth and grooved patterned surfaces are shown in Figure 8, 9 respectively.

![Confocal image of smooth patterned surface showing usual self assembly of water droplets into hexagonal array leading to honey comb structure](image)

Figure 8: Confocal image of smooth patterned surface showing usual self assembly of water droplets into hexagonal array leading to honey comb structure

This difference in pattern formation on the grooved surface can be explained through the underlying principle of moving contact lines, pinning of droplets and the discontinuity of energy minimum on a grooved surface. Provided the droplet size is larger than the groove width, for a parallel grooved surface with grooves infinitely long and close to each other, there can be movement of contact line which lies at an angle to the grooves. This results in the formation of droplets having a local structure (metastable state) due to the
Figure 9: Confocal image of grooved patterned surface showing hexagonal array of smaller droplets inside hexagonal ring like pattern (scale bar: 100 micrometer)

continuous displacement of contact line without any pinning.

The ring formation is attributed to the moving three-phase contact line and change in its direction due to pinning of droplets at certain points and successive evaporation of droplets. On the grooved surface, there are spaces for occupying new droplets. This favours renucleation at the spaces inside the ring. This confirms that the difference in pattern is attributed completely to the geometry of the underlying surface.

The grooves in DVD are comparable to a capillary with a number of grooves normal to the axis and as indicated in the theory, the argument of contact line moving is valid for this order of length scale. Such a pattern has not been observed with 1D grooves separated by 50 µm \[^7\]. The same pattern as seen above was observed in non-aqueous environment also i.e. ethanol was used instead of water. The images of ungrooved and grooved surfaces patterned in ethanol environment is shown in Figure[10][11] respectively.

The water contact angle of the surfaces before and after patterning are given in Table[1] and Figure[12]. The increase in contact angle of approximately 30 degrees was observed. This increase in hydrophobicity is attributed to the change in surface roughness and also the interfacial energy of the surfaces.
Figure 10: Confocal image of ungrooved patterned surface patterned in ethanol environment also shows usual self assembly of water droplets into hexagonal array leading to honey comb structure

The fact that the droplets are in a Wenzel state was confirmed by upturning the substrate with water droplet and noting the properties of the pendant drop. It was observed that the droplet sticks to the surface which confirms the high adhesiveness of droplet with the surface. The images of the droplets are shown in Figure 14, 15

The variation of contact angle with the change in droplet radius for all the patterned and unpatterned surfaces are measured and shown in Figure 13 and Table 2. It is observed that there is no considerable variation in contact angle

Table 1: Contact angle of the substrates before and after patterning

| Substrate                          | Contact angle (in degrees) |
|------------------------------------|---------------------------|
| Bare ungrooved                     | 74.77                     |
| Bare grooved                       | 86.88                     |
| Patterned ungrooved (water)        | 110.00                    |
| Patterned grooved (water)          | 104.00                    |
| Patterned ungrooved (ethanol)      | 116.00                    |
| Patterned grooved (ethanol)        | 104.00                    |
Figure 11: Confocal image of grooved patterned surface patterned in ethanol environment showing hexagonal array of smaller droplets inside hexagonal ring like pattern with increasing droplet volume. This also shows that the drops are sticking to the surface showing Wenzel’s state of wetting. For further confirmation, contact angle hysteresis were performed and all showed a high contact angle hysteresis indicative of Wenzel’s state. The data is shown in Figure 16.

5 Conclusion

For the first time, two different sides of compact disc, planar and grooved surfaces, were patterned using the breath figure approach both in aqueous and ethanol environments. Under optimized conditions, honey comb patterns were obtained on the planar substrate and a dual pattern consisting of smaller droplet clusters inside a distorted hexagonal like ring on the grooved substrate. Increase in roughness of any substrate is known to increase the hydrophilicity of already hydrophilic surfaces and hydrophobicity of hydrophobic surfaces. Wetting studies confirmed the increase in roughness of the patterned surfaces in both cases. In the present case, the increase in roughness due to the patterns leads to increased hydrophobicity of the substrates. Large hysteresis in contact angle confirmed that the water penetrated into the pores exhibiting Wenzel state of wetting. The honey comb pattern is attributed to
the combined effects of thermocapillary convection and the presence of air film between the droplets. The dual pattern is a pattern resulting from the movement and de-pinning of contact line due to 1D boundary conditions.

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Table 2: Variation of contact angle with droplet volume

| Liquid drop volume | bare grooved | bare ungrooved | patterned grooved | patterned ungrooved |
|--------------------|--------------|----------------|-------------------|---------------------|
| 1                  | 84.2         | 80.9           | 99.4              | 110.7               |
| 2                  | 76.9         | 85.3           | 94.2              | 108.8               |
| 3                  | 76.6         | 88.7           | 95.7              | 109.3               |
| 4                  | 74.8         | 89.3           | 96.6              | 110.3               |
| 5                  | 75.2         | 85.6           | 98.3              | 111.3               |
| 6                  | 75.1         | 83.1           | 97.0              | 110.7               |
| 7                  | 75.3         | 81.6           | 98.4              | 109.8               |
| 8                  | 75.3         | 79.2           | 98.3              | 109.9               |
| 9                  | 75.1         | 78.7           | 99.6              | 110.6               |
| 10                 | 74.9         | 79.7           | 99.3              | 110.7               |

Figure 14: Images showing high adhesive force of surface to water: Ungrooved patterned surface with droplet turned upside down

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Figure 15: Images showing high adhesive force of surface to water: Grooved patterned surface with droplet turned upside down

Figure 16: Contact angle hysteresis of the substrates

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