Electronic Supplementary Material (ESI) for Soft Matter.

Supplementary information

Uni-, Bi- and Tri- Directional Imbibition of Water and Oils on a Chemically Patterned Silicon Micropillar Array

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Free energy of the imbibition front:

Here we derive the equations for the graphs 2e and 2f in the main text. As explained in the main text, a uniform wall instead of a row of micropillars is assumed. In addition, we assume that the shape of the meniscus is a straight line that touches the top of the previous row of pillars, and some spot x in the space between the pillar rows. This configuration is the one with the lowest surface energy, as either convex or concave curved meniscus would only have increased liquid-vapor surface energy with other parameters staying the same. This meniscus configuration is shown in Fig. 2a and 2c.

We mark as x the distance of the meniscus from the pillar row, so that x = 0 μm means the meniscus has not advanced at all from the pillar row and x = 20 μm means that the meniscus makes contact with the next pillar row, leading to the imbibition front advancing.

The surface free energy can then be written as:

$$U = w\gamma\sqrt{h^2 + x^2} - xw\gamma cos\theta - hw\gamma cos\theta, \qquad \text{(S1)}$$

where w is the width of the imbibition front, h the height of the pillars and θ the contact angle. The first term is the liquid-vapour surface energy, the second term is the liquid-solid surface energy term that comes from the contact of the meniscus with the horizontal bottom surface and the third term the liquid-solid surface energy from the contact of the liquid with the vertical walls of the pillars.

We then set d = 10 μm so that in the advancing direction, $\theta = \theta_1$ for 0 μm < x < 10 μm, and $\theta = \theta_2$ for 10 μm < x < 20 μm. In the equilibrium direction, $\theta = \theta_2$ for 0 μm < x < 10 μm, and $\theta = \theta_1$ for 10 μm < x < 20 μm. We also drop the third term from the total surface energy calculation since it does not depend on x and would be an unnecessary constant in the potential energy.

The total surface energy per unit length in the advancing direction is:

$$U(x)/w = \gamma(\sqrt{h^2 + x^2} - xcos\theta_1), \text{ 0 μm < x < 10 μm,} \qquad \text{(S2)}$$

$$U(x)/w = \gamma(\sqrt{h^2 + x^2} - 10\ \mu m * cos\theta_1 - (x - 10\ \mu m)cos\theta_2), \text{ 10 μm < x < 20 μm.} \qquad \text{(S3)}$$

The total surface energy per unit length in the equilibrium direction is:

$$U(x)/w = \gamma(\sqrt{h^2 + x^2} - xcos\theta_2), \text{ 0 μm < x < 10 μm,} \qquad \text{(S4)}$$

$$U(x)/w = \gamma(\sqrt{h^2 + x^2} - 10\ \mu m * cos\theta_2 - (x - 10\ \mu m)cos\theta_1), \text{ 10 μm < x < 20 μm.} \qquad \text{(S5)}$$

The derivatives of S2-S5 are respectively:

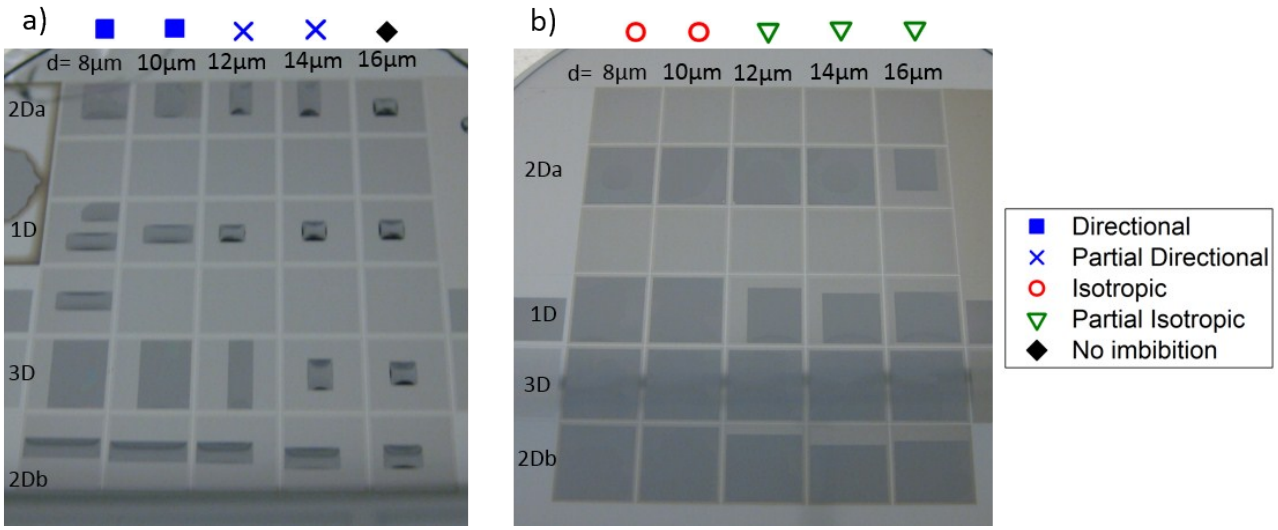
$$d(\frac{U(x)}{w})/dx = \gamma(\frac{x}{\sqrt{h^2 + x^2}} - cos\theta_1), \text{ 0 μm < x < 10 μm,} \qquad \text{(S6)}$$

$$d(\frac{U(x)}{w})/dx = \gamma(\frac{x}{\sqrt{h^2 + x^2}} - cos\theta_2), \text{ 10 μm < x < 20 μm.} \qquad \text{(S7)}$$

$$d(\frac{U(x)}{w})/dx = \gamma(\frac{x}{\sqrt{h^2 + x^2}} - cos\theta_2), \text{ 0 μm < x < 10 μm,} \qquad \text{(S8)}$$

$$d(\frac{U(x)}{w})/dx = \gamma(\frac{x}{\sqrt{h^2+x^2}} - cos\theta_1)$$, 10 µm < x < 20 µm. (S9)

Directional imbibition types:

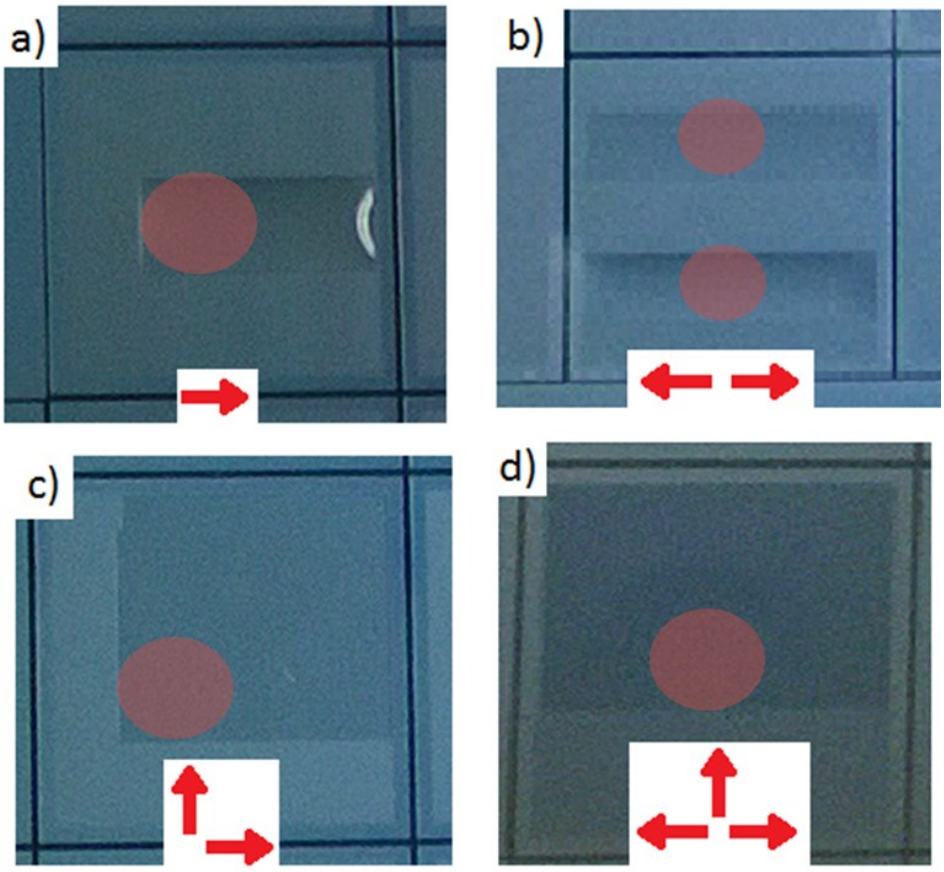


Supplementary Figure S1. End states of spontaneous directional imbibition experiments. Each figure represents 5 experiments (the columns) with different values of d. Each experiment with a given set of parameters looked at the four possible directional imbibition types (the rows). These figures correspond to the lowest row (a) and the third highest row (b) of Fig. 4 in the main text.

a) The parameters are h = 11.3 µm, ϑ_1= 39°. With d values of 8 µm and 10 µm, all four directional imbibition types fill as intended, and the experiment is classified as "directional". In the experiments with d values 12µm and 14µm, the imbibition has proceeded into several of the intended directions, but pinned to others, so the experiment is classified "partial directional". The experiment with d = 16 µm has only rectangular droplets, with no imbibition to any direction, so the experiment is classified "no imbibition".

b) The parameters are h = 16.1 µm, ϑ_1= 33°. In the experiments with d values 8 µm and 10 µm, all structures are filled completely so the experiment is classified as "isotropic". With d values between 12 µm and 16 µm, the structures are mostly completely filled, with only some of the intended dry directions unfilled, so the experiment is classified "partial isotropic",

Directional imbibition of water:



Supplementary Figure S2. Directional imbibition of water a) Unidirectional, b) Bidirectional (2Db), c) Bidirectional (2Da), d) Tridirectional. For all images, the parameters are h= 18.5 µm, s= 20 µm, $\theta_1 = 52°$, $\theta_2 = 0°$. *The parameter d is 8 µm in a) and d), and 10 µm in b) and c).*

Supplementary videos:

Supplementary Video S1. 1D filling process. The parameters are: d = 8µm, h = 12.5 µm and the liquid is a 2:1 mixture of hecadecane and dodecane.

Supplementary Video S2. 2Da filling process. The parameters are: d = 8µm, h = 12.5 µm and the liquid is hexadecane. Only first 5 seconds of the filling process are shown.

Supplementary Video S3. 2Db filling process. The parameters are: d = 8µm, h = 12.5 µm and the liquid is hexadecane.

Supplementary Video S4. 3D filling process. The parameters are: d = 8µm, h = 12.5 µm and the liquid is hecadecane. Only first 5 seconds of the filling process are shown.