Wetting Morphologies at Structured Surfaces

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Many experimental methods have been developed by which one can prepare chemically and/or topographically structured substrates. If one deposits a certain amount of liquid on such a substrate, one experimentally observes a large variety of wetting morphologies.

Some years ago, we started to classify the possible morphologies at *chemically* structured surfaces theoretically. We discovered that these surfaces lead to *morphological wetting transitions* at which the wetting layer changes its shape in a characteristic and typically abrupt manner **[1, 2]**. We extended this work (i) to liquid channels or filaments with freely moving endcaps which leads to a morphology diagram with a line of discontinuous transitions that ends in a critical point **[3]**, see biannual report 2002+2003, (ii) to nucleation at circular surface domains which is characterized by an activation free energy with two maxima **[4]**, (iii) to vesicle adhesion at striped surface domains **[5]**, and (iv) to a general stability analysis of these morphologies **[6]**.

In the context of nonplanar substrates, we first studied chemically heterogeneous and *topographically* rough surfaces for which we derived the general functional relationship between contact angle, interfacial tensions, and line tension **[7]**. More recently, we considered topographically structured surfaces which contain surface channels (or grooves) and obtained a complete classification for the corresponding wetting morphologies **[8]**. The following contribution will focus on this latter work.

Open Systems for Micro- and Nanofluidics

An obvious prerequisite for "labs-on-a-chip" miniaturized labs are appropriate micro-compartments for the confinement of very small amounts of liquids and chemical reagents. Like the test-tubes in macroscopic laboratories, these micro-compartments should have some basic properties: They should have a well-defined geometry by which one can measure the precise amount of liquid contained in them; they should be able to confine *variable* amounts of liquid; and they should be accessible in such a way that one can add and extract liquid in a convenient manner.

An appealing design principle for such microcompartments is based on open and, thus, directly accessible surface channels which can be fabricated on solid substrates using available photolithographic methods. The simplest channel geometry that can be produced in this way corresponds to channels with a rectangular cross section. The width and depth of these channels can be varied between a hundred nanometers and a couple of micrometers.

Classification of Wetting Morphologies

As shown in our recent study **[8]**, liquids at surface channels can attain a large variety of different wetting morphologies including localized droplets, extended filaments, and thin wedges at the lower channel corners. Examples for these morphologies as observed by atomic (or scanning) force microscopy (AFM) are shown in **Fig. 1**.

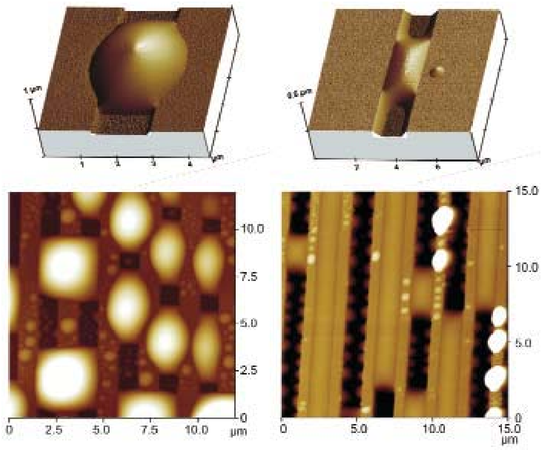

Fig. 1: Atomic (or scanning) force microscopy images of liquid morphologies on silicon substrates with rectangular surface channels which have a width of about one micrometer. On the left, the liquid does not enter the channels but forms large lemon-shaped droplets overlying the channels (dark stripes). On the right, the liquid enters the channels and forms extended filaments separated by essentially empty channel segments (dark stripes).In the bottom row, one sees several parallel surface channels in both images; in the top row, there is only one such channel with a single droplet (left) or filament (right). Close inspection of the upper right image reveals (i) that this filament is connected to thin wedges along the lower channel corners and (ii) that the contact line bounding the meniscus of the filament is pinned to the upper channel edges.

When the AFM experiments were first performed, it was not known how to produce a certain liquid morphology since there was no systematic theory for the dependence of this morphology on the materials properties and on the channel design. Such a theory has now been developed. Our theory addresses the strong capillary forces between substrate material and liquid and takes the 'freedom' of contact angles at pinned contact lines into account. Such a contact line is visible in the upper right image in **Fig. 1**. For this contact line, which is pinned along the channel edges, the contact angle θ_p is not determined by the classical Young equation but can vary over the range

$$\theta \leq \theta_p \leq \theta + \pi/2 \qquad (1)$$

for a surface channel with rectangular cross section where θ denotes the contact angle on all planar segments of the substrate surface (taken to be chemically homogeneous). An analogous 'freedom' is also found for those contact lines that are pinned to the boundaries of chemically defined surface domains as first emphasized and explored in our previous work **[1]**.

The classification described in **[8]** is based (i) on general considerations such as the relation given by (1), (ii) on analytical shape calculations which are feasible for relatively simple morphologies such as liquid filaments with constant cross section, see **Fig. 2**, and (iii) on numerical minimization of the liquid's free energy which leads to constant mean curvature surfaces. A surprising prediction of our theory is that the experimentally observed polymorphism of the wetting liquid depends only on two parameters: (i) the aspect ratio X of the channel geometry, i.e., the ratio of the channel depth to the channel width; and (ii) the contact angle θ which characterizes the interaction between substrate material and liquid.

The corresponding morphology diagram, which is displayed in **Fig. 3**, represents a complete classification of all possible wetting morphologies.

Inspection of this figure shows that one has to distinguish seven different liquid morphologies which involve localized droplets (D), extended filaments (F), and thin wedges (W) at the lower channel corners.

For microfluidics applications, the most important morphology regime is (F^-) which corresponds to stable filaments. Since this regime covers a relatively small region of the morphology diagram, see **Fig. 3**, it can only be obtained if one carefully matches the channel geometry described by its aspect ratio *X* with the substrate wettability as described by the contact angle θ.

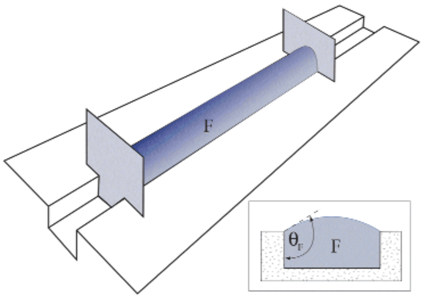

Fig. 2: Liquid filament (F^+) with positive Laplace pressure, i.e., with a meniscus that is curved upwards away from the substrate. The filament is located within the rectangular surface channel and is "sandwiched" between two pistons which provide walls orthogonal to the long axis of the filament. The contact angle at these walls is $\pi/2$ which ensures that the filament has constant cross-section and is bounded by a cylindrical meniscus. In mechanical equilibrium, the total force exerted by the filament onto each piston must vanish. The inset shows the filament cross section and the associated filament angle $\theta_p = \theta_F$ which is uniquely determined by the aspect ratio X of the surface channel and the contact angle θ of the substrate material.

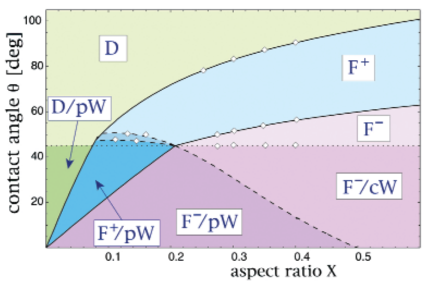

Fig. 3: Morphology diagram as a function of the aspect ratio X of the channel and the contact angle θ which characterizes the interaction between substrate material and liquid. This diagram contains seven different morphology regimes which involve localized droplets (D), extended filaments (F), and thin wedges (W) in the lower channel corners. The diagram represents a complete classification of all possible wetting morphologies and should be universal, i.e., should apply to other liquids and substrate materials as well.

Perspectives

One relatively simple application of the morphology diagram shown in **Fig. 3** is obtained if the system is designed in such a way that one can vary or switch the contact angle in a controlled fashion. One such method is provided by electrowetting; alternative methods, which have been recently developed, are substrate surfaces covered by molecular monolayers that can be switched by light, temperature, or electric potential. If one varies the contact angle by one of these methods, the system moves in the morphology diagram parallel to the vertical axis. It can then cross the boundary between the two morphology regimes (F^-) and (F^+). This transition leads to a controlled variation in the length of the liquid filament: these filaments enter the surface channels with decreasing contact angle but recede from these channels with increasing contact angle as has been demonstrated by electrowetting experiments.

The theory underlying the morphology diagram in **Fig. 3** predicts that this diagram is rather universal and applies to many different systems. The experiments described in **[8]** use a polymeric liquid that freezes quickly and can then be scanned directly with the tip of an atomic force microsope.

The morphology diagram should also apply to other liquids and other substrate materials. It should also remain valid if one further shrinks the surface channels and, in this way, moves deeper into the nanoregime. As one reaches a channel width of about 30 nanometer, one theoretically expects new effects arising from the line tension of the contact line, but such nanochannels remain to be studied experimentally.

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