LIQUID PINNING ON NANOMETRIC STEPS DURING THE DEWETTING OF A THIN POLYSTYRENE FILM ON ALUMINA

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Recent years have seen an increasing interest in strategies to control and manipulate small quantities of liquids. The rapid development of microfluidics is an example of such technologies at micrometer scale. Other techniques such as dip pen lithography [1] or liquid nanodispensing [2, 3] have shown their efficiency to pattern surfaces at nanometer scale. Scaling down these techniques as much as possible requires a good understanding of wetting processes at nanometer scale. Nevertheless, the laws governing the spreading of liquids on surfaces are well understood at the macroscopic scale [4] but little is known on the limit under which these laws do not hold anymore. In order to address this problem we studied the dewetting of a polystyrene film on alumina α (0001). After annealing at 1500°C during 3 hours, the surface exhibits parallel terraces of about 1 μm separated by nanometric steps. When a polystyrene film is spin coated on this surface it dewets by nucleation and growth of dry holes. We show that the study of the dynamics of the contact line and, in particular, its interaction with the steps of the surface used as model defects is a simple way to probe the behavior of the contact line at nanometer scale.

Macroscopic considerations based on the equilibrium contact angle allow to predict that the downward steps of the surface should anchor the contact line and stop its motion whereas upward steps should have no effect on the contact line motion. Steps should therefore drastically modify the contact line dynamics resulting in an asymmetric dewetting.
We performed dewetting experiment of polystyrene thin films deposited by spin coating on alumina. In the case of metastable films (thicker than 15 nm) [5], the dewetting process could be nucleated by making a hole in the film with the AFM tip. This allows a very precise control of the location of the hole with respect to the alumina steps and thus a study of the interaction of the liquid front with a given step.
Figure 1 shows an AFM image obtained during the growth of a dry hole on the surface when nucleated on a series of terraces with heights in the 3-10 nm range. We observe that the hole has the shape of a truncated circle. One side was blocked by the first downward step while the other side propagated on the upward steps like on a homogeneous surface. This result confirms the behavior predicted from a simple macroscopic description.
In order to estimate the limit of validity of these arguments, we performed the same experiment on sub-nanometric steps. In this case the liquid is insensitive to the steps and the hole grows symmetrically (figure 2). Statistics over a large number of steps show that a minimal step height is necessary to anchor the contact line. Using different polymer molecular weights, we found that this critical size is equal to about 3 times the radius of gyration of the polymer. This means that the “macroscopic” behavior is valid down to dimensions of the order of the diameter of the fluid particles. It gives an estimation of the amplitude of the fluctuations of the contact line.

This result has important consequences from a fundamental point of view, in particular for the understanding of the wetting on real surfaces with defects, which is characterized by a contact angle hysteresis. For applications, it also shows that nanometric features can modify or stop the spreading of a liquid or introduce an asymmetry on the wetting properties of a surface. This may be interesting for the design of new devices.

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References:

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Figures:

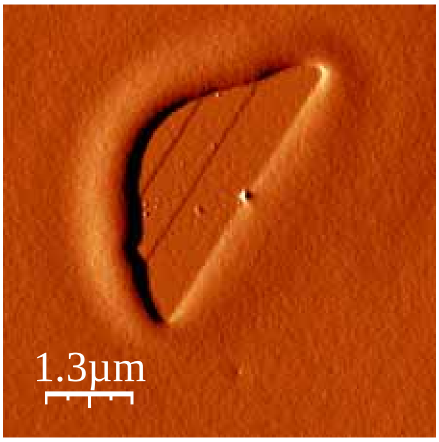

Figure 1 : *AFM image of a dry hole growing on a series of terraces 3-10 nm high. The rim around this hole is anchored on a downward step (to the right) whereas it develops rising the steps (to the left)*

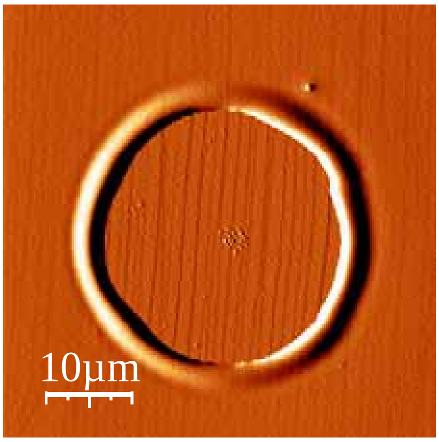

Figure 2 : *AFM image of a dry hole growing on a series of sub-nanometric terraces. In this case the dewetting is isotropic, insensitive to the surface features.*