Contact angle hysteresis at the nanometer scale studied with CVD-prepared carbon cones attached toAFM tips

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Introduction

Despite numerous studies published over the last decades [1], the wetting mechanism of real surfaces remains difficult to understand and describe properly, especially considering microscopic and nanoscopic scales. The most characteristic phenomenon of non-ideal surfaces wetting lies in the contact angle which is no longer unique, but varies through a range of values, creating a contact angle hysteresis. This hysteresis is assumed to find its origin in the pining of the contact line on surfaces defects. Most of the studies already published used surfaces patterned with few tens of micrometer-wide defects [2]. Recently, Ramos et al extended these studies down to 200 nm defects [3]. These results allowed describing accurately the effect of defect concentration and spatial repartition on the contact angle hysteresis, but a description of the pinning on individual nanometric defects was still lacking.

We propose here an original approach which consists in studying, by atomic force microscopy (AFM), the capillary force exerted on cone-shaped carbon tips dipped in liquids. The quasi 1D geometry of these tips is ideal to study isolated defects. Those tips also benefit from the fact that their surface is homogeneous and therefore exempt of hysteresis. Our set-up enabled investigating individual nanometric defects and observing how the contact angle hysteresis builds from the isolated defects.

Experimental

We used carbon cones grown from chemical vapour deposition onto carbon nanotubes [4-6] mounted on an AFM tip [7] to measure the force exerted by the liquid on the dipped part of the cone. We thus duplicated, at nanometer scale, the Whilelmy plate method which is a standard technique to measure macroscopic contact angles. The liquid was deposited in the form of droplets of approximately 20 µm in diameter using a micromanipulator and a micro-injection device. Using a manual approach, we dipped the tip of the carbon cone in the liquid and measured by AFM the capillary force the tip was subjected to during approach-retraction cycles.

Results and Discussion

Comparing the overall shape of the force curves and the cone profile reconstructed through TEM characterizations (see Figure 1), we could estimate advancing and receding contact angles on the cone surface of glycerol and heptadecane respectively, as already demonstrated in literature using a carbon nanotube [7] or an Ag_2Ga nanowire [8].

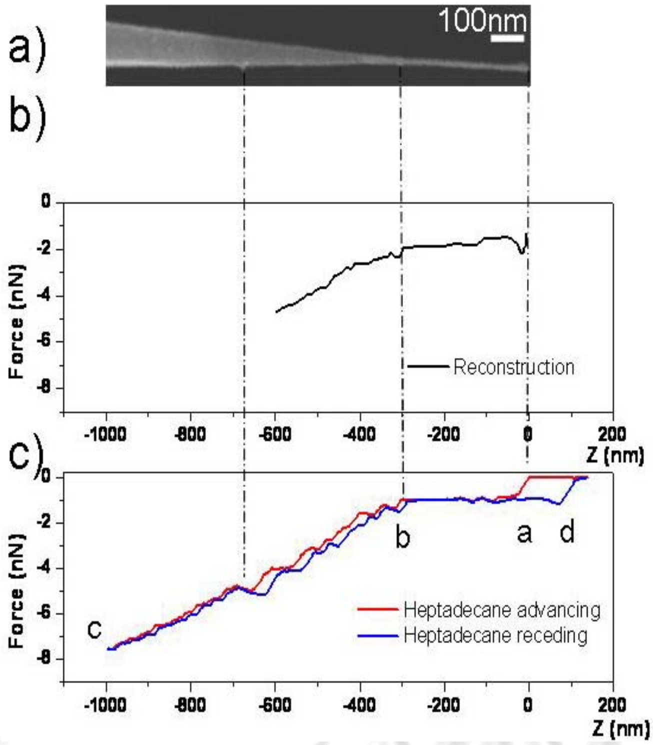

Fig. 1 a) FEG-SEM micrograph of one of the carbon-cone tip used as a capillary force probe. The far tip (on the right) is cylindrical because it corresponds to the nanotube used to deposit the carbon cone onto it. **b)** Reconstruction of the theoretical force applied on the probe. **c)** Capillary force measurement (red: dipping-in, and blue: dipping-out) in heptadecane.

In addition to the overall shape of the force curve, we observed local variations of the capillary force characteristic of the interaction of the contact line with nano-sized isolated defects, resulting –or not– in the pining of the line. By observing force measurements on small portions of the tip, such as displayed on Fig. 2 (top), one can distinguish isolated defects of two types. The first one, quoted (a), induces a hysteresis cycle, resulting from the pining then de-pining of the contact line on this defect. On the second type of defect, (b), we observe a variation of the force which is fully reversible and therefore does not show any hysteresis. These two behaviours are very well described by a pioneer model proposed by Joanny and de Gennes [7] which distinguished “strong” and “weak” defect regimes by equilibrating the defect force with the elastic capillary force.

Our results constitute the first experimental evidence of weak defects which do not take part in the building of the surface hysteresis. In the strong defect regime, we could evaluate the dissipated energy per defect and propose a simplified model which was verified quantitatively. Interestingly, on nanometer-sized defects, the dissipated energy is as small as 10^{-20} J which is very close from the kT limit.

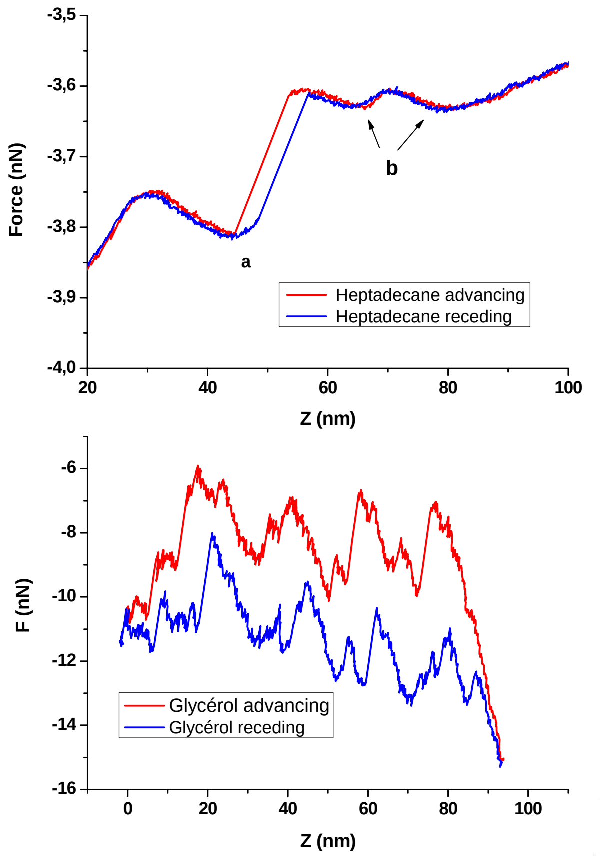

Fig. 2: (top) The effects of strong defect (a) and weak defect (b) discriminate, **(bottom)** Typical curves displaying the opening of collective hysteresis cycles, that is to say the contact angle hysteresis.

We also proposed an estimation of the critical height of a topographic defect corresponding to the transition from weak to strong defects. We found a value in the order of nanometer for heptadecane and in the order of Å for glycerol. This is in agreement with the fact that we could observe weak defects for heptadecane only, while both kind of defects, weak or strong, generate strong pinning with glycerol.

The previous example displayed isolated defects, observed on rather smooth parts of the probe. Considering areas of the carbon cone with higher density of defects, the behaviour of the contact lines changed with this density. When strong defects happened to be close enough to each other, their hysteresis cycles merged together resulting in the opening of larger cycles. The larger and closer the defects, the larger the cycles they induce. This is the evidence that, when defects are dense enough, their interaction gives rise to the separation of the advancing and receding force, hence to the contact angle hysteresis. A quantitative correlation between contact angle hysteresis and defects density is underway.

Conclusions

The use of carbon cones as force probes has allowed the behaviour of the liquid to be observed at nanometre scale, and then the wetting phenomena at this scale to be understood. It is now possible to probe the mechanical properties of the liquid contact line, whose precise structure remains mostly unknown. Not only this study allows having a deeper look at the interaction of a single defect with the liquid line, but it also demonstrates how the interaction between strong defects creates the contact angle hysteresis. Moreover, this work could help understanding the creation of nanomeniscus observed in contact-mode AFM measurements in ambient conditions, and also the wetting behaviour of carbon nanotubes in a variety of situations such as filling experiments, filtration by aligned nanotubes membranes, impregnation of nanotube by liquid matrice precursors, etc.

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