## Decrease of the adhesion force with vapor pressure

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Experimental evidence of a monotonous decrease of the capillary forces between hydrophilic surfaces with increasing relative humidity from 0 to 100% is presented. In concordance with the results of a theoretical simulation, we identified the objects' shape as the origin of different adhesion force vs. RH behaviours when treating with nanoscale objects. If the water neck is formed between a flat surface and a nanometric object presenting a truncated cone shape the adhesion force decreases with increasing vapour pressure. The variety of meniscus force behaviours found for different shapes emphasizes the importance of geometry in capillary phenomena at the nanometric scale.

Moisture alters the cohesion among particles in powders and the adhesion of particles to surfaces. The principal reason for this effect is the formation of a liquid neck or meniscus at the contact region between particles or between the particles and the surface. The attractive force caused by such a liquid meniscus is called "capillary force" and it generally predominates (for hydrophilic surfaces) over other surface forces under ambient conditions [1]. A profound understanding of capillary forces is essential in the studies of the behaviour of powders and soils [2], friction, hydrophobic interactions, and has implications in industries as pharmaceutical (colloid stability, suntan creams), food engineering (the cleaning of food) [3], and new materials (coatings, lubricants).

Atomic Force Microscopy (AFM) allows for the investigation of adhesion forces between bodies of micro or nanometer sizes and plays, therefore, a major role in the studies of capillarity. In this study, AFM experiments were performed using sharp as well as dull Si tips and flat mica surfaces. Adhesion force vs. environmental water pressure curves were obtained by measuring force vs. distance curves (from which adhesion forces were extracted) [4] while increasing the relative humidity slowly from 0 to 100%. In order to preserve small tip apex dimensions very low normal loads have been applied. When using sharp Si tips the adhesion force decreases monotonously with increasing water vapour pressure (Fig. 1, left), while it shows a maximum behaviour when using larger (> 15nm) tips (not shown here). While the maximum behaviour has been reported reiterately [1, 5-11], we found no reference to a strict decrease of the adhesion force with increasing humidity in literature.

A simple model explaining the experimental findings has been developed, based on a previously described model [12], using continuum theory and the formation of minimum energy water necks. The model suggests that, when bringing a hydrophilic nanoscale object in proximity to a hydrophilic surface the object's shape is a decisive factor for determining the adhesion behaviour with humidity. While conical shapes present increasing  $F_{adh}$  vs. H curves, sharp and nearly flat caps yield decreasing curves (Fig. 1, right). Curved tips, in turn, show the well known force curves displaying a maximum.

Experimental and theoretical results are consistent if we assume that the "small" tips, preserved up to what the SEM can elucidate, exhibit a nanometer sized flat surface free of asperities. The Nanosensors Si tip is likely to exhibit a flat surface after entering into first contact with the stiff mica sample since Nanosensors Si cantilevers are aligned parallel to the <110> direction [13] (thus the <110> direction is perpendicular to the cone axis) along which cracks are easily propagated resulting in a nearly perfectly flat fracture surface [14].

The results imply that the undesirable sticking effect between surfaces occurring at increasing relative humidity could be avoided by controlling the shape of the surface asperities at the nanometric scale. Furthermore, for a correct interpretation of AFM adhesion maps the tip size and shape have to be taken into account – hydrophilic samples do not necessarily yield a

capillary force increase with increasing moisture.

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## **Figures:**

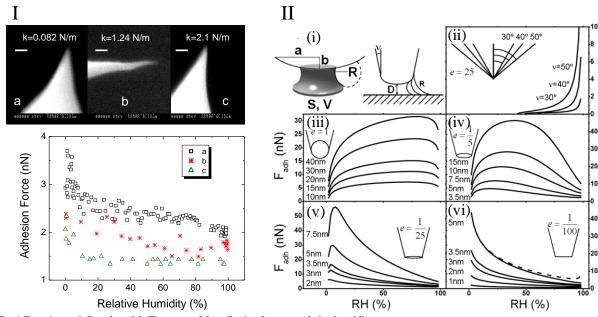


Fig. 1 Experimental (I) and model (II) curves of the adhesion force vs. relative humidity. Top left (I): SEM images showing three tips after they had been used to measure the adhesion force with flat mica surfaces (the scale bar represents 60 nm). Bottom left (I): adhesion force as a function of the relative humidity for the three sharp Si tips. Nominal tip radii are 7 nm for (a) and (c) and 2 nm for (b). II, (i) Scheme of the modelled tip geometry and water meniscus (ii-vi)  $F_{adh}$  vs humidity curves calculated with the ellipsoid model (D = 0.2 nm) for different values of the tip apex form factor e = b/a (= 25, 1, 0.2, 0.04 and 0.01, respectively) and the ellipsoid transverse semi axis a. In (b) we show the results for a quasi conical tip (b/a = 25, a = 5 nm) for different aperture angles. In (iii-vi) solid lines are results for tips with  $v = 10^{\circ}$  and different a (curve labels correspond to a values used). In (vi) the dashed line corresponds to a quasi-truncated tip with a = 5 nm and  $v = 30^{\circ}$ .