

Supplementary information :

Description of the models used in the simulation for the tip-sample interaction forces.

The equation of motion in ambient dynamic AFM can be approximated, to its first mode^{S1}, to

$$m \frac{d^2 z}{dt^2} + \frac{m\omega}{Q} \frac{dz}{dt} + kz = F_{ts} + F_0 \cos \omega t \quad (1)$$

where k is the spring constant, Q is the Q factor, ω is the drive frequency (here always equal to the natural frequency), $m=k/\omega^2$ and F_0 is the amplitude of the drive force. A net tip-sample force F_{ts} that reproduces standard behavior in ambient AFM in the presence of water films can be written in terms of the tip-sample distance d ^{S2,S3}. Similar expressions are used here for the tip-hydrophilic sample interaction. In F_{ts} different forces are considered:

$$F_{ts} = F_a + F_{AD} + F_{CAP} + F_{DMT} \quad (2)$$

where F_a states for the long range attractive London dispersion force. F_{AD} takes into account both the adhesion force due to the formation of capillary neck and mechanical adhesion. F_{CAP} is the capillary force when the capillary neck is formed and F_{DMT} is the contact repulsive force according to the Derjaguin Muller Toporov model

In the long range the attractive London dispersion force F_a is (tip-hydrophilic sample interaction)

$$F_a(d) = -\frac{H_w R}{6d_w^2} \quad d > d_{\text{off}} \text{ (tip retraction) and } d > d_{\text{on}} \text{ (tip approach)} \quad (3)$$

H_w is the Hamaker constant corresponding to the hydrated tip-hydrated surface interaction, R is the tip radius, d_w is an effective distance of interaction $d_w = d - 2h$ ^{S3}; h is the height of the water films on the tip and sample's surfaces. There is a metastable region $d_{off} > d > d_{on}$ where the capillary neck might form. If the capillary forms (3) can be identified with the adhesion force F_{AD} ^{S3}

$$F_{AD}(d) = \frac{F_{Doff} - F_{Don}}{d_{off} - d_{on}}(d - d_{on}) + F_{Don} \quad d_{off} > d > d_{on} \quad (4)$$

where

$$F_{Don} = -\frac{R}{6a_0^2} \left[\frac{H_w - H}{d_{off} - a_0}(d_{on} - a_0) + H \right] \quad (5)$$

and

$$F_{Doff} = -C_{off} \frac{RH_w}{6a_0^2} \quad C_{off} \geq 0 \quad (6)$$

where H is the Hamaker constant for the tip and the sample interaction, a_0 is an intermolecular distance and C_{off} controls the decay in the adhesion force. Here $C_{off} = 0.3$ has been used here throughout. In the region $a_0 < d < d_{on}$ the adhesion force is written as

$$F_{AD}(d) = -\frac{H^* R}{6a_0^2} \quad a_0 < d < d_{on} \quad (7)$$

where

$$H^* = \frac{H_w - H}{d_{off} - a_0} (d - a_0) + H \quad (8)$$

When mechanical contact occurs $d \leq a_0$ the adhesion force is

$$F_{AD} = -\frac{HR}{6a_0^2} = -4\pi R\gamma \quad d \leq a_0 \quad (9)$$

where γ is the surface energy. When the capillary neck is formed the capillary force is

$$F_{CAP}(d) = -\frac{2\pi\gamma_w R}{1 + \frac{\pi d^3}{V_{men}}} \quad \text{provided capillary on and } d > a_0 \quad (10)$$

where γ_w is the surface energy of water and V_{men} is the volume of the meniscus forming the water bridge. It should be noted that $H_w \approx 24\pi(a_0)^2\gamma_w$ and $H \approx 24\pi(a_0)^2\gamma$.^{S4} When $d \leq a_0$, the distance d is replaced by a_0 in (10). Furthermore V_{men} is calculated using geometrical considerations

$$V_{men} = 4\pi R h^2 + \frac{4}{3}\pi h^3 \quad (11)$$

The distance d_{on} has been taken to be $d_{on} = 3h$.^{S3} d_{off} can be calculated numerically by solving the Laplace-Young equation^{S5}

$$d_{off} \approx V_{men}^{1/3} - \frac{1}{5R} V_{men}^{2/3} \quad (12)$$

Finally, when contact occurs, i.e. $d \leq a_0$, the repulsive force is written, from the Derjaguin Muller

$$\text{Toporov (DMT) model}^{S6} \quad F_{DMT}(d) = \frac{4}{3} E^* \sqrt{R} \delta^{3/2} \quad d \leq a_0 \quad (13)$$

where E^* is the effective elastic modulus of the contacting bodies and δ is the sample deformation, i.e. $\delta = a_0 - d$. The schemes representing the different interaction regimes when the capillary neck is formed at the required separation, i.e. $d = d_{on}$, are shown in Fig. 1. Note that if the capillary neck forms the interaction is relatively large, i.e. affects the amplitude reduction, for separations as large as $d \sim d_{off}$ which might range from 3-6 nm depending on the amount of water on the surfaces. This is the most critical aspect that might induce great losses of apparent height according to our simulations.

It should be noted that while water might be present on both the tip and/or the sample, the capillary neck might not form; whether it forms or not largely depends on temperature and relative humidity, and possibly frequency.^{S7} The scenario in which the capillary neck does not form even when water layers are present has also been modeled here and a scheme for this case is also shown in Fig. 1. The attractive forces in this case are

$$F_a = -\frac{H_w R}{6d_w^2} \quad d_w > a_0 \quad \text{or} \quad d > 2h + a_0 \quad (14)$$

$$F_{AD} = -\frac{H^* R}{6a_0^2} \quad d_w < a_0 \quad \text{or} \quad d \leq 2h + a_0 \quad (15)$$

where

$$H^* = \frac{H_w - H}{2h}(d - a_0) + H \quad (16)$$

and, finally, in the contact

$$F_{AD} = -\frac{HR}{6a_0^2} \quad d \leq a_0 \quad (17)$$

The repulsive force is also used here (12). For the tip-hydrophilic sample, whether the capillary neck forms or not, the parameters are: $k=2\text{N/m}$, $f=f_0=70\text{kHz}$ ($w=w_0=2\pi f_0$), ($E_t=120\text{ GPa}$ (Young modulus of the tip), $E_{s(\text{mica})}=60\text{ GPa}$ (Young modulus of the mica), $R=7\text{ nm}$, $\gamma=7\text{ mJ}$, $\gamma_w=10\text{ mJ}$ and $a_0=0.165\text{ nm}$. The value of h is varied in the simulations from 0.2 to 1 nm in order to establish relationships between the amount of water present on the surface and the apparent height. The actual values are given while discussing the results and/or in the figures where the results are presented.

When the hydrophobic sample is present the capillary neck cannot form because there can be no water on its surface. As stated, the hydrophobic sample protrudes a distance L above the dry

surface of the hydrophilic supporting surface (here mica). In order to take this phenomenon into account, the interaction, for the long range we write (here $d_w=d-h$)

$$F_a = -\frac{H_w R}{6d_w^2} \quad d_w > L + a_0 \quad \text{or } d > L + h + a_0 \quad (18)$$

$$F_{AD} = -\frac{H^* R}{6a_0^2} \quad d_w < L + a_0 \quad \text{or } d \leq L + h + a_0 \quad (19)$$

where

$$H^* = \frac{H_w - H}{h} (d - a_0) + H \quad (20)$$

and, finally, in the contact

$$F_{AD} = -\frac{HR}{6a_0^2} \quad d \leq L + a_0 \quad (21)$$

Again, the repulsive force in (12) has been used here with the appropriate value of elastic modulus. Note also that since the hydrophobic sample is protruding a height L , the indentation needs to be modified to $\delta = a_0 + L - d$. For the hydrophobic sample E_s (Stearic Acid) = 10 GPa (Young modulus of the stearic acid). Furthermore, viscoelasticity might also be present in the tip-sample

inertaction, in particular when the sample is a polymer or relatively compliant samples such as SAMs.^{S8,S9} In this respect the Kelvin-Voigt model has been used as

$$F_{\eta} = -\eta(R\delta)^{1/2} \dot{\delta} \quad (22)$$

where δ is the instantaneous deformation, $\dot{\delta}$ is the tip velocity during deformation and η is the viscosity of the materials in contact. Here $\eta = 1000$ Pa·s throughout.

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