Electronic Supplementary Material (ESI) for Nanoscale

Supporting Information for:

Three-dimensional quantitative force maps in liquid with 10 piconewton, angstrom and sub-minute resolutions

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Force reconstruction in bimodal AFM

The method developed by Katan *et. al*[1] to reconstruct the interaction force from amplitude modulation data is applied by using the data corresponding to the first mode (A_{01}>>A_{02}). In Katan's approach, the interaction force between tip and sample at a distance d is given by

$$F_{ts}(d) = 2k\int_d^{\infty}\left[\left(1+\frac{A(u)^{1/2}}{8\sqrt{\pi(u-d)}}\right)\Omega(u)-\frac{A(u)^{3/2}}{2\sqrt{(u-d)}}\frac{d\Omega(u)}{du}\right]du \qquad (1)$$

where Ω is given by

$$\Omega(u) = \frac{\omega}{\omega_0}\left(1+\frac{A_d}{A(u)}\cos\phi(u)\right)-1 \qquad (2)$$

and A_d is given by the

$$A_d = \frac{A_0}{\omega^2}\sqrt{\left(\omega_0^2-\omega^2\right)^2+\left(\frac{\omega\omega_0}{Q}\right)^2} \qquad (3)$$

where A_0, Q, k, ω, ω_0 are, respectively, the free amplitude, quality factor, spring constant, driving frequency and resonant frequency of the first mode of the cantilever.

For applying Eq. (1), it is necessary to calculate the behavior of Ω and A with the distance. The dependence of the amplitude and the phase-shift on the piezo displacement z_c is directly measured in 3D-AFM at every pixel of the xy plane. A translation in the z-axis must be made in order to set the axis origin. We assume that the amplitude starts to decay when z_c is approximately equal to the free amplitude of the cantilever. In addition, it is necessary to turn these curves into amplitude and phase-shift versus minimum distance curves. The minimum distance between tip and sample is estimated as

$$d = z_c + z_0 - A \qquad (4)$$

where z_0 is the average deflection.

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Examples of amplitude and phase-shift distance curves and the force reconstruction processes are shown in Fig. S1.

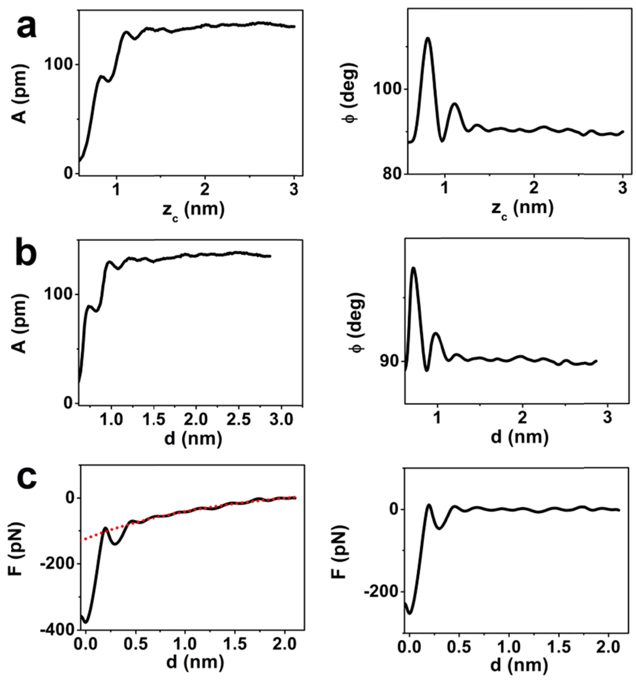

Figure S1. Figure S1 shows different stages in the method used to reconstruct the interaction force. a, A_1 and ϕ_1 vs. piezo-displacement z_c curves are recorded at every pixel in a bimodal 3D-AFM experiment. b, The above curves are transformed into A_1 and ϕ_1 *vs.* distance *d* curves. c, Application of Katan's force reconstruction method to the curves shown in b. The long range tail of the interaction force is fitted and subtracted from the total force.

In bimodal AFM the contrast depends on the observable

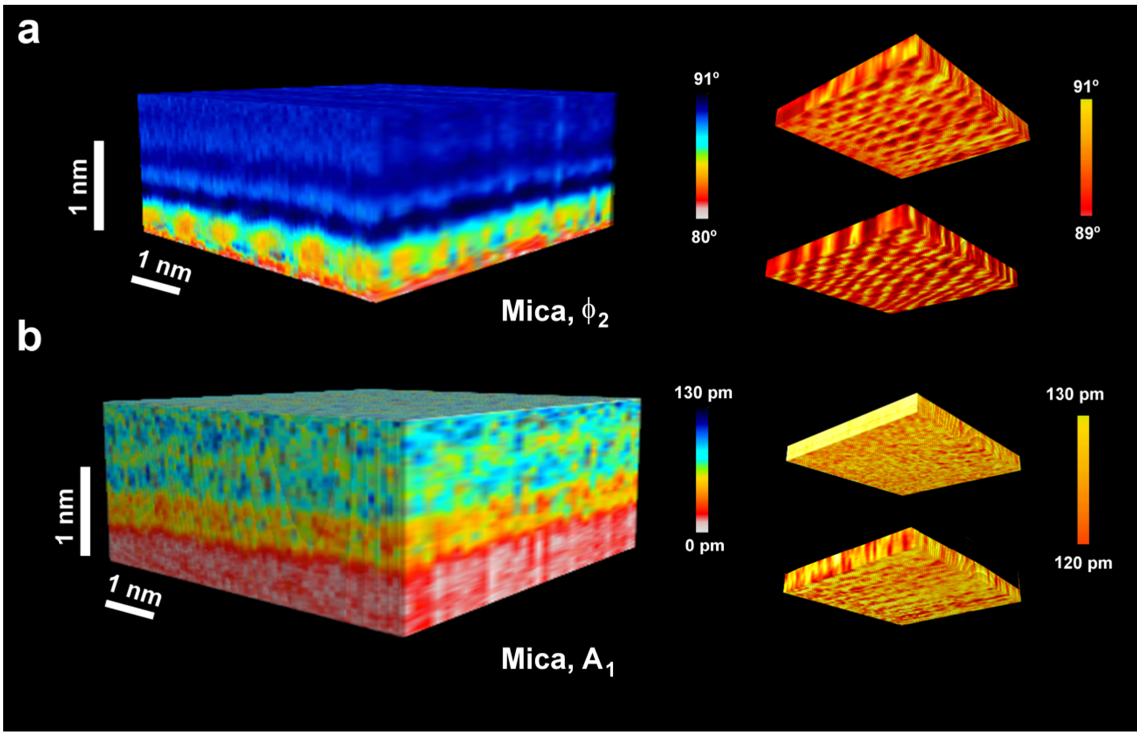

Figure S2. 3D images of solid-water volumes on mica. (a) Side (left) and perpendicular (right) views of a 3D image plotting ϕ_2 data. The side view shows two hydration layers on mica. The contrast observed in the ϕ_2 data enables to resolving atomic-resolution features on the mica surface. The right panels shows an atomic resolution image of a deformed mica surface (bottom) and of the first hydration layer (top). (b) Side and perpendicular views of the 3D plotting A_1 data acquired simultaneously with (a). This image provides less information about the interface that the phase shift data. In particular, the lower signal-to-noise ratio in A_1 (right panel) does not show atomic resolution.

References

1. Katan, A. J.; van Es, M. H; Oosterkamp, T. H. *Nanotechnology* **2009** , 20, 165703