SUPPLEMENTARY MATERIALS

Surrogate models for studying the wettability of nanoscale natural rough surfaces using molecular dynamics

Lingru Zheng[1], Maja Ruecker[1], Tom Bultreys[2,3], Apostolos Georgiadis[4,1], Miranda M. Mooijer-van den Heuvel[4], Fernando Bresme[5], J.P. Martin Trusler[1], Erich A. Müller[1]

[1] Department of Chemical Engineering, Imperial College London, U.K.

[2] ProGRess/UGCT, Department of Geology, Ghent University, Belgium

[3] Department of Earth Science and Engineering, Imperial College London, U.K.

[4]Shell Global Solutions International B.V., Amsterdam, Netherlands

[5]Department of Chemistry, Imperial College London, U.K

1. AFM BACKGROUND NOISE EVALUATION

We evaluate the impact of background noise and imaging velocity by calibrating the measurements over an atomically flat surface. Hence, a freshly cleaved muscovite was chosen and measured in QITM (Quantitative imaging with the NanoWizard 3 AFM) mode with the JPK-instrument at Imperial College London; the same equipment used for measuring the Ketton carbonate sample used in the main work. An example of the resulting image is displayed in Fig. S1, showing that the corresponding noise ranges between 0 pm and 800 pm, meaning quality features larger than 800 pm in the z-coordinate would be well recognized.

We also analyzed the artefacts which often occur as the experiments approaches atomic resolution. Fig. S2 illustrates that this artefact may be associated with the angle at which tip approaches the surface. This artefact makes it difficult to assess the noise level. In the images obtained this can exceed 5 nm at some locations.

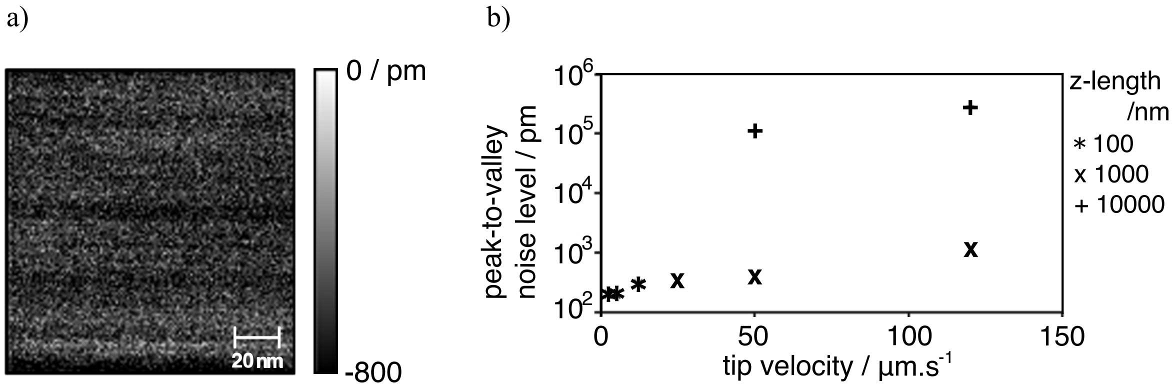


Figure S1 a) shows the image of the muscovite surface at a tip velocity of 120 µm.s^{-1} and z-length of 1000 nm. The noise level is 800 pm, which is 4 times larger than the molecular structure of muscovite. b) shows the noise level for different tip velocities and z-lengths. Only with a tip velocity of 2.5 µm.s^{-1} atomic resolution may be achieved. A higher z-length results also in a higher noise level.

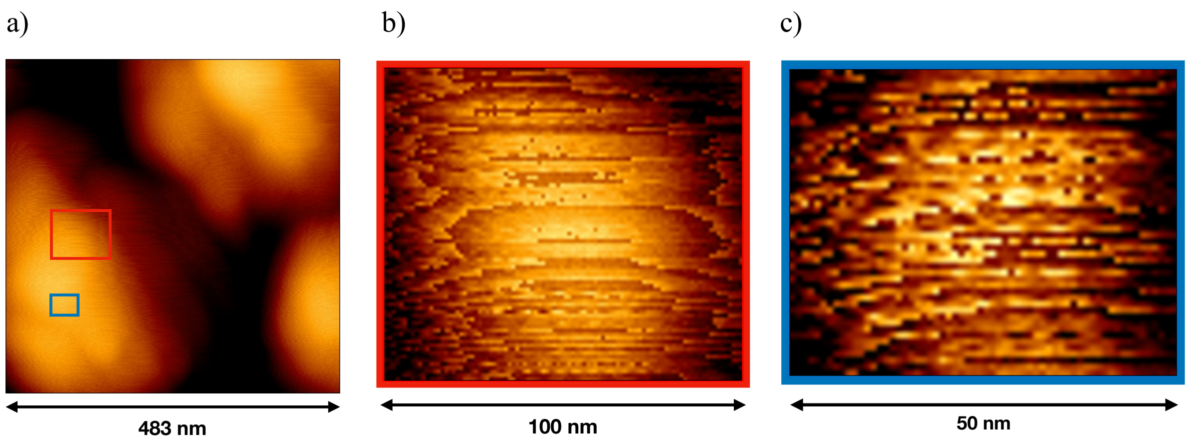


Figure S2 a) AFM image with a resolution of 512 × 512 pixel (left). The images in red and blue rectangles are zoomed-in to show that the surface structure may be responsible for the artefact since it appears on b) steep surfaces, whereas not on c) horizontal surfaces.

2. FOURIER TRANSFORM SHOWING THE SPATIAL OSCILLATION PERIOD OF THE SURFACES

The computation is carried out on randomly selected horizontal (*x*), vertical (*y*) and diagonal lines of the AFM data in Fig. 1c to obtain the frequency distribution of the spatial oscillation period in each dimension. Fig. S3 shows the highest frequency occurs at wavelengths (Λ) of 7.55 nm (32 grid lengths) and 5.66 nm (24 grid lengths).

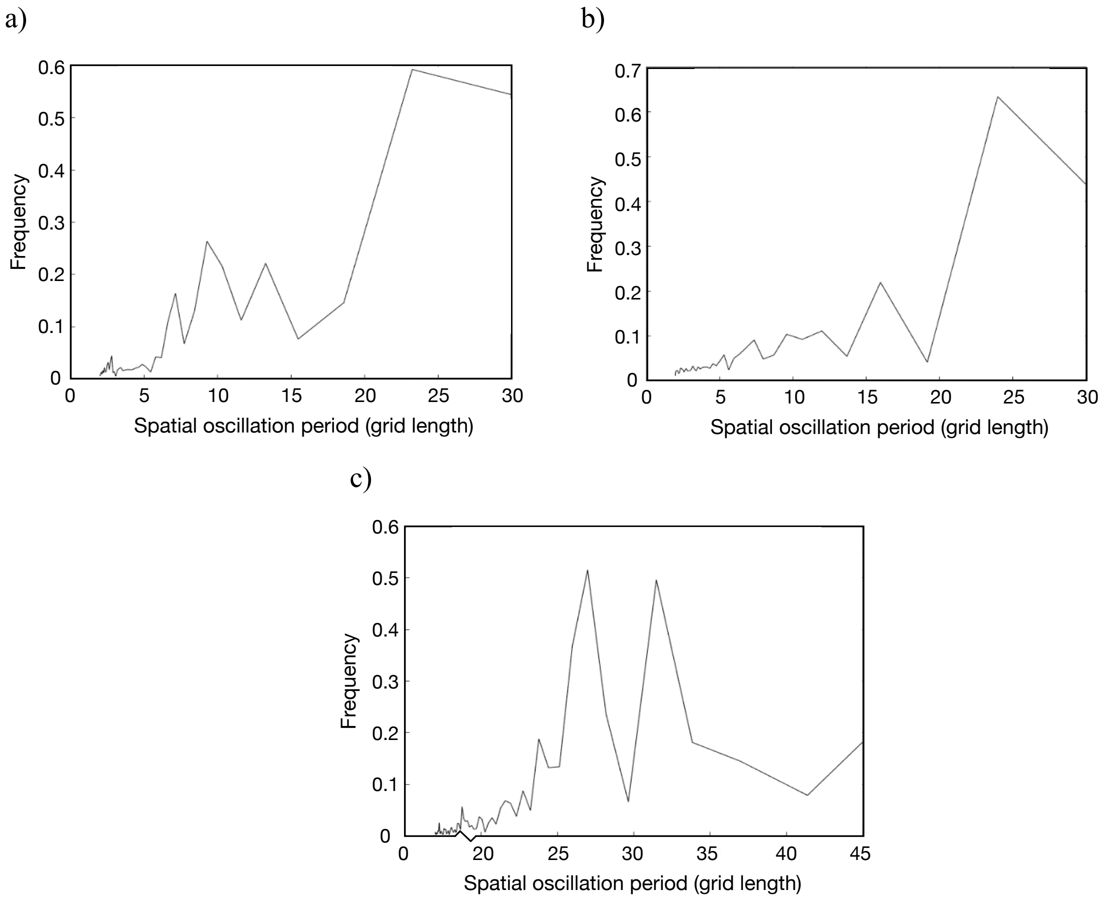
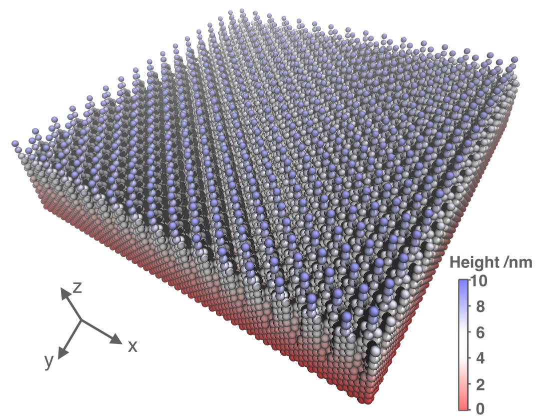


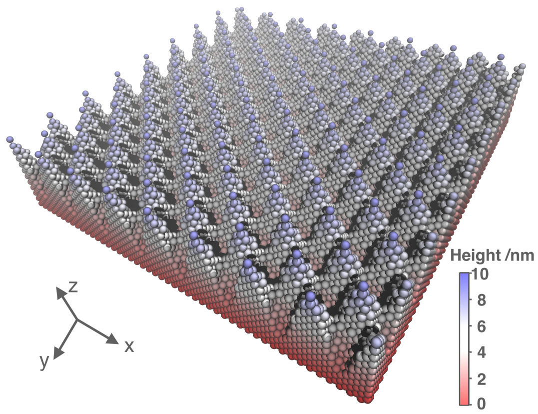
Figure S3 Spatial oscillation period distribution of the selected lines of AFM data in the a) horizontal (*x*), b) vertical (*y*) and c) diagonal dimensions.

3. FIGURES OF SURROGATE MODEL SURFACES

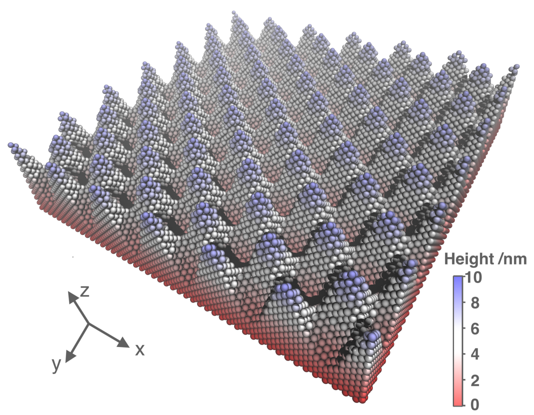
a) Λ = 1.416 nm (6 grid lengths)



b) Λ = 2.832 nm (12 grid lengths)



c) Λ = 3.776 nm (16 grid lengths)



d) Λ = 5.664 nm (24 grid lengths)

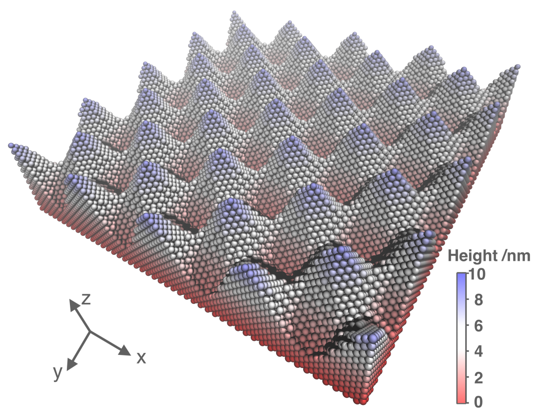
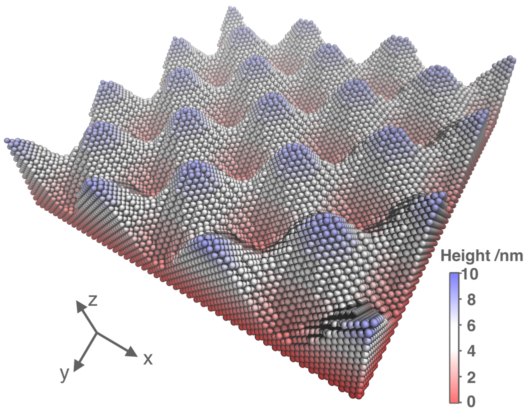
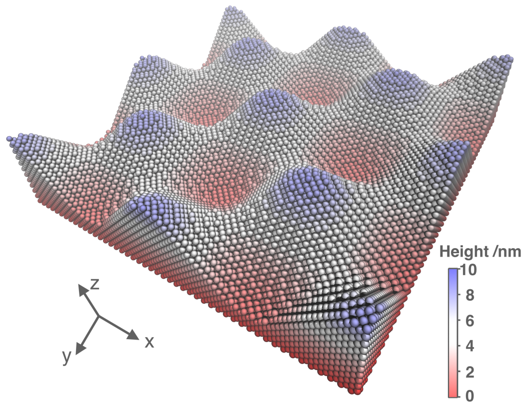


Figure S4 Eight sinusoidal surfaces with 4 nm amplitude and wavelength (Λ) from 1.416 nm to infinity. These surfaces are constructed in the same way and have the same base area as the surface in Fig. 2b. The wavelength range covers the wavelengths of Fig. 2b characterized using Fourier transform. The color of the beads indicate their elevations (in nm) in the z-direction. The color bars are displayed on the right of the surfaces.

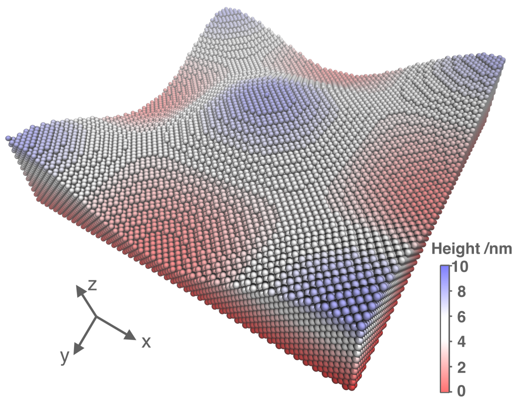
e) Λ = 7.552 nm (32 grid lengths)



f) Λ = 11.328 nm (48 grid lengths)



g) Λ = 22.656 nm (96 grid lengths)



h) $\Lambda = \infty$ nm (flat)

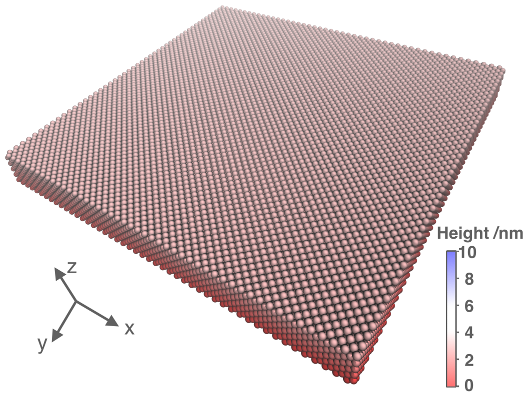


Figure S4 (continued) Eight sinusoidal surfaces with 4 nm amplitude and wavelength (Λ) from 1.416 nm to infinity. These surfaces are constructed in the same way and have the same base area as the surface in Fig. 2b. The wavelength range covers the wavelengths of Fig. 2b characterized using Fourier transform. The color of the beads indicate their elevations (in nm) in the z-direction. The color bars are displayed on the right of the surfaces.

4. NUMBER OF FRAMES NEEDED FOR EVALUATING CONTACT ANGLES

A size-related factor investigated is the number of frames extracted from the simulation trajectory that is used to compute the contact angle and curvature after the system has reached equilibrium. The system domain in each frame is split into voxels, and the number density within each cell is computed to identify the fluid or solid region. Inputting more frames enables us to capture more comprehensively the dynamics of the droplet hence result in a more accurate average contact angle or curvature. We collect the equilibrated frames at a 50 ps interval. Fig. S3 shows the frame number effect on the fluid contact angle over a flat surface. We chose to use 100 frames when computing the droplet contact angles and curvatures. The choice maximizes the accuracy of the results since, with 100 frames, the results approaches the case where 50000 fluid molecules are simulated in the system. Besides, the decision only made the post-processing time to increase moderately in comparison with, for instance, using 10 frames.

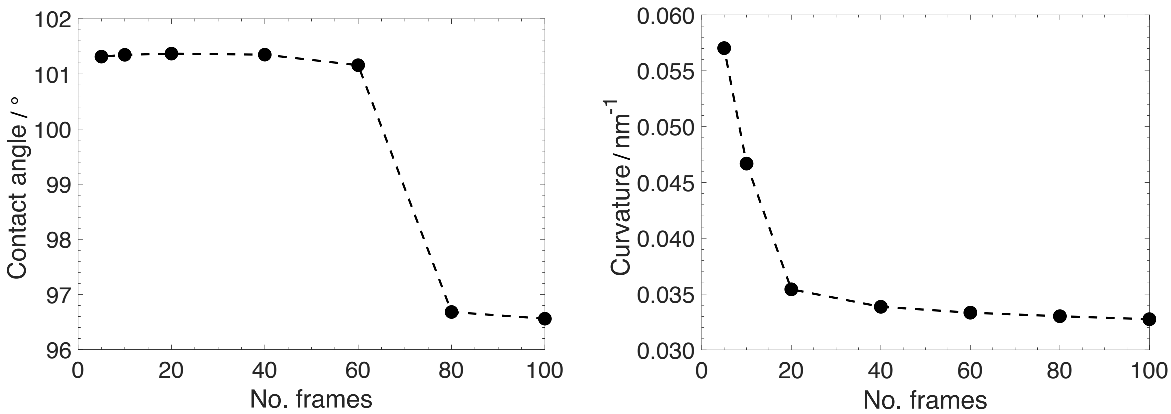


Figure S5 Number of simulation frames input in contact angle and curvature computation. Dashed lines are guide to the eye.

5. VISUALIZATION OF DROPS ON SURFACES

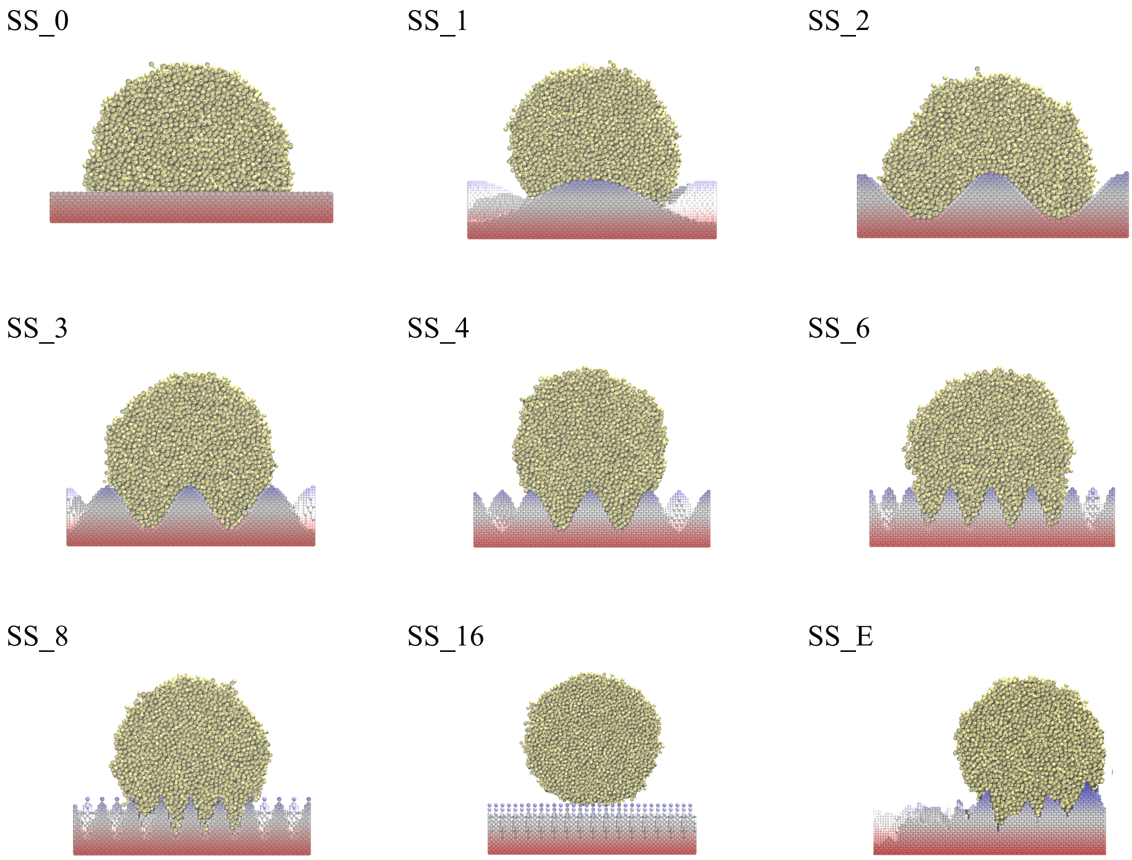


Figure S6 Longitudinal section of an equilibrated configuration. Surfaces defined in Table 1 (c.f. Figure 9)

6. AFM FORCE MAPPING AND QI-MODE

This section briefly describes the force mapping technique employed and how it differs from other modes of operation such as the contact mode and the tapping mode.

In “contact mode” the tip continuously tracks the surface height. In this mode, the lateral deflection due to height differences, may lead to imaging artefacts such as stripes making this technique unsuitable for measurements for rough surfaces or substrates with strong adhesion[1] . On flat surfaces, however, contact mode is the technique suited best for atomic resolution. The horizontal tip movement allows to obtain scanning speed which exceed thermal drift. These measurements need to be conducted with a soft probe (<1 N/m) showing large responses to small variations. The samples is usually placed in liquid or vacuum to prevent jump-in effects potentially altering the surface at the atomic level[2,3], but can be also done in in air[4,5].

The tapping mode, refer to the technique in which the cantilever is oscillated close to resonance frequency. Though the tapping mode is not as sensitive to lateral forces as the contact mode, artefacts such as stripes may still occur[6]. Due to the angle with which the tip approaches and retract from the surface, the path of the tip movement needs to be considered. Furthermore, height variations larger than the chosen amplitude within short distances may cause problems. Tapping mode has been utilized to reach atomic resolution. It is specially, suitable for surfaces which are soft or show large attraction to the tip as the oscillation can prevent jump-in effects (non-contact mode). The tips used for this method are stiff (> 1000 N/m) and measurements are conducted in vacuum or liquid to prevent capillary effects on the tip[2]. For this measurement, quick movement is essential to exceed thermal drift, therefore only low amplitudes can be used.

On rough surfaces, force mapping, in which each point is approached strictly vertical and retracted following the same path as opposed to horizonal as in contact mode or with an angle as in tapping mode, is the best option. In this mode, the topographical images are complemented with a force-distance curves for each pixel. With this method the distance the of the tip approach and retract as well as the force applied can be controlled. However, these measurements take a long time. JPK instruments has developed an enhanced force mapping technique (QI™ mode) with a tip movement algorithm which controls the exact x-y position during a force-distance measurement, but allows to overshoot in z when moving to the next point, leading to a faster imaging as illustrated in Figure S7. This technique allows the measurement of height, stiffness and adhesion directly and in parallel and to introduce own functions also as full force distance curve is recorded for each data point[7] .

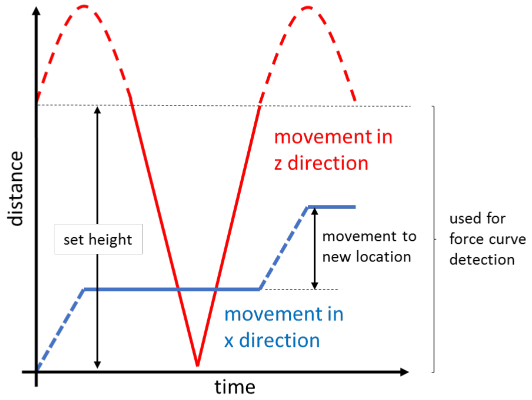


Figure S7 In QI^{TM} mode the tip does not move in x-y direction while a force distance curve is obtained. Yet, the movement algorithm allows an overshoot above the set z-distance, which enables a fast data acquisition (adapted from [7]).

At the current stage, we are not aware of any study demonstrating atomic resolution with this mode. We conducted experiments on freshly cleaved mica in air, which is known to be atomically smooth with surface features of 200 pm height[8] to assess the quality of this measurement. Figure S8 demonstrates that for low amplitude and tip velocities, the noise level arrives exactly at this value. The reason that it appears as random noise rather than an atomic structure is likely due to thermal drift, which exceeds the low velocity of the tip in this mode.

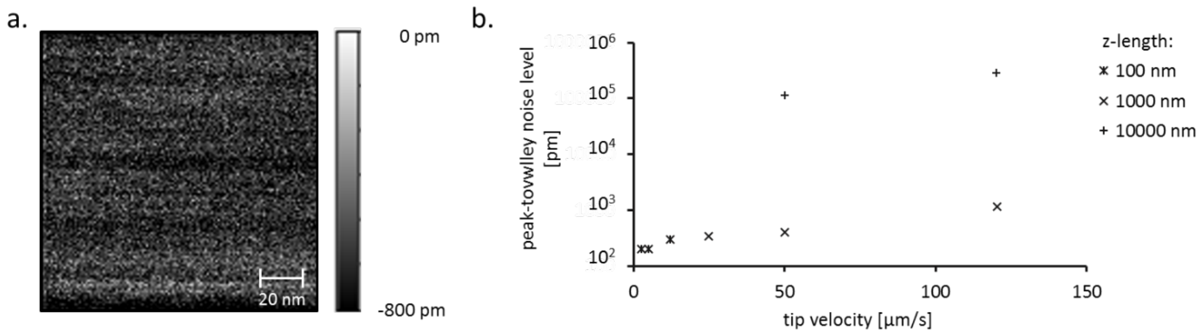


Figure S8 (a) Image of the muscovite surface at a tip velocity of 120 µm/s and z-length of 1000 nm. The noise level is 800 pm, which is 4x larger than the molecular structure of muscovite. (B) Noise level for different tip velocities and z-lengths. Only with a tip velocity of 2.5 µm/s atomic resolution may be achieved. A higher z-length results also in a higher noise level.

Figure S9 displays a force distance curve measured on the Ketton rock surface in air in presence of a nano-scale water. The blue line reflects the approach and the red line the disengage. The approach clearly displays the jump into contact with the surface. The attraction towards the surface the cantilever experience, is due to a thin water layer. Once the hydrophilic tip contacts the fluid-fluid interface it becomes dragged towards the surface. The contact point is being defined when the tip bends back into the original position. This illustrates that the impact of nano-scale water layers on the true height can be neglected when measuring with QI-mode.

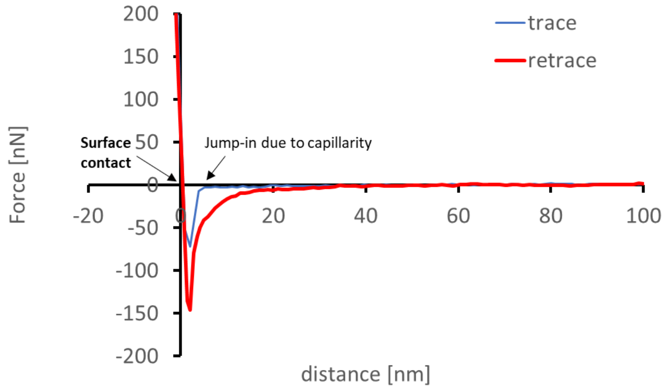


Figure S9 Force distance curve obtained at a Ketton rock surface in presence of water. The jump-in occurs once the hydrophilic tip contacts the fluid-fluid interface and bends the tip towards the surface. The height of the surface is detected when the tip starts to bend into the opposite direction.

Even though from all imaging modes QI-modes is best suited for rough surfaces, a few imaging artefacts are unavoidable, one of which is the impact of the tip shape. AFM probes can have a spherical, parabolic or pyramidal tip. Further, the tips may vary in length and sharpness, which is usually described through the tip radius. For sharp tips, the vendor usually guarantees for the tip tip to be below a specific radius and gives an average value. The true tip size is unknown and may also be altered during the measurement. On rough surfaces, the tip shape and sharpness, defines, whether the tip is able to reach the surface directly below it or is stopped by side walls as illustrated in Figure S10. This can happen at all length scales, where the general tip shape is limiting (III) and at small scale, where the tip radius, is key (II). In general, this artefact will cause the surface to look flatter than it is. This artefact can be identified through the increased adhesion force obtained at this point, as the contact area between side walls of the tip is larger and therewith the amount of interactions between the solid and the tip.

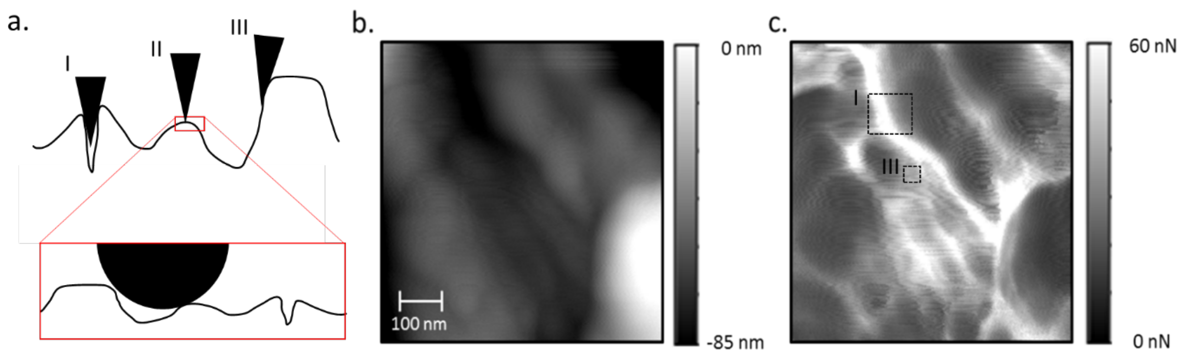


Figure S10 (a) limited reach of the tip due to surface roughness on varying length scales (I,II) and tip sliding (III). In the height image (b) these locations may be assigned an incorrect height. On larger scale these locations can be identified due to the increased adhesion in the adhesion image, due to the increased contact area between tip and surface (c). On smaller scale, this effect is unavoidable. Therefore, the smaller scale surface structure can only be obtained were larger scale surface roughness does not need to be considered and were the surface is parallel to the x-y oriented piezoelectric actuators. In general, the roughness measured with AFM is therefore always underestimated.

This also holds for another artefact often observed: tip sliding. Depending on the force settings and the angle with which the tip lands on the surface, the tip may also bend to the side causing a lateral deflection. The leaning of the tip towards the side causes an inaccurate height detection, but can be also identified due to increased adhesion of the side walls (Figure S1). This effect is also strongest on steep surfaces. On surfaces parallel to the X-Y orientation of the horizontally aligned piezoelectric actuators, this effect can be minimized by choosing the appropriate force.

7. REFERENCES

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