

Supporting information

Liquid cell of AFM

The AFM is of the sample-scanning type. The sample is mounted on the piezo scanning element via a sample holder made of PEEK (an inert plastic), that sticks into the fluid cell in which the experiments are performed. This fluid cell (depicted in figure S1) exposes only inert materials to the fluid and is thoroughly cleaned before and after each experiment. The tip is electrically grounded. Control of the microscope is done with CAMERA electronics and software (Leiden Probe Microscopy B.V.).

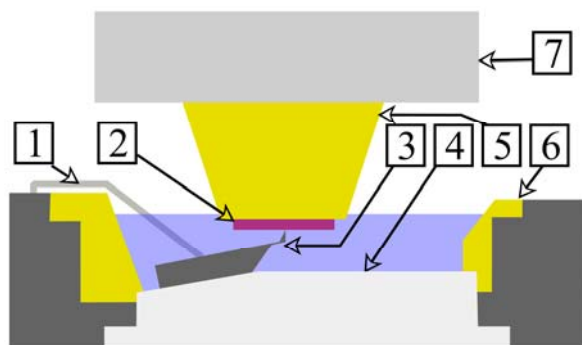


Figure S1

Figure S1 Fluid cell in which the experiments were performed. Legend: 1) Stainless steel spring. 2) Sample. 3) AFM cantilever chip. 4) ZeroDur glass window for detection laser. 5) PEEK sample holder. 6) PEEK ring to prevent contact between liquid and outer body. 7) Piezo scanner

Nanobubbles

Nanobubbles were first introduced as explanation for long-range jumps of attractive forces seen in Surface-Forces Apparatus measurements by Parker *et al*¹. Since then, a great number of SFA and AFM force measurements, as well as AFM images have shown evidence of nanobubbles². The 2003 review of Attard³ gives a good overview of these. More recent work by Zhang *et al*⁴ shows a systematic investigation of nanobubble properties under different circumstances, and Agrawal *et al*⁵ have demonstrated control over the size and position of bubbles by micropatterning of polymers. Smeets *et al*⁶ find these bubbles inside solid-state nanopores. Although the evidence for their existence by now is overwhelming, the origin of the stability of nanobubbles is still unclear. From the point of view of thermodynamics, the high Laplace pressure inside the bubbles should drive them to dissolve into the liquid within milliseconds. In AFM measurements, they are seen to be stationary over minutes or even hours by many of the aforementioned authors. Meyer *et al*⁷ report that the formation of bubbles is triggered by capillary cavitation after contact in their SFA experiment, and that they disappear in a few seconds when the surfaces are separated. All these studies of nanobubbles involve inherently invasive techniques, since they bring two surfaces close together. Often, it is difficult to determine whether the bubbles pre-existed on the surface or were generated by the proximity of the second surface, either by cavitation upon separation or spontaneously by spinodal dewetting. Zhang and co-workers⁸ conclude from a combination of AFM measurements and infrared spectroscopy that CO₂ nanobubbles can preexist on hydrophobic surfaces if these were covered with ethanol before being exposed to water. These bubbles have a thickness less than 80 nm but radii of curvature of at least 2 μm . Recent experiments using x-ray⁹ and neutron¹⁰ reflectivity measurements on single surfaces provide strong evidence against the pre-existence of nanobubbles at the interface between water and methyl-terminated SAMs on quartz and silicon substrates. Instead, the authors of these papers propose the existence of a homogeneous depletion layer at the SAM/water interface, with a thickness comparable to one molecular

diameter. Using smooth surfaces covered by defect-free SAMs that have no pinning sites for bubbles, and a non-invasive measurement technique are mentioned as important prerequisites for attaining this result. But to do a measurement of the forces between two surfaces, invasive methods are inevitable. Studying the effects of nanoscale heterogeneity on surface forces therefore requires a technique that either does not generate nanobubbles, or circumvents them.

Bubbles and domain sizes. To verify the sample preparation, and inspect domain sizes, dynamic mode imaging was performed in air and in pure water. Two different sets of SAM samples can be distinguished. A number of samples incubated for 16-24 hours showed an even coverage with SAM domains of 30-80 nm in diameter (figure S2a). When these samples were immersed in water, a large number of nanobubbles could be seen on the surface (figure S2b).

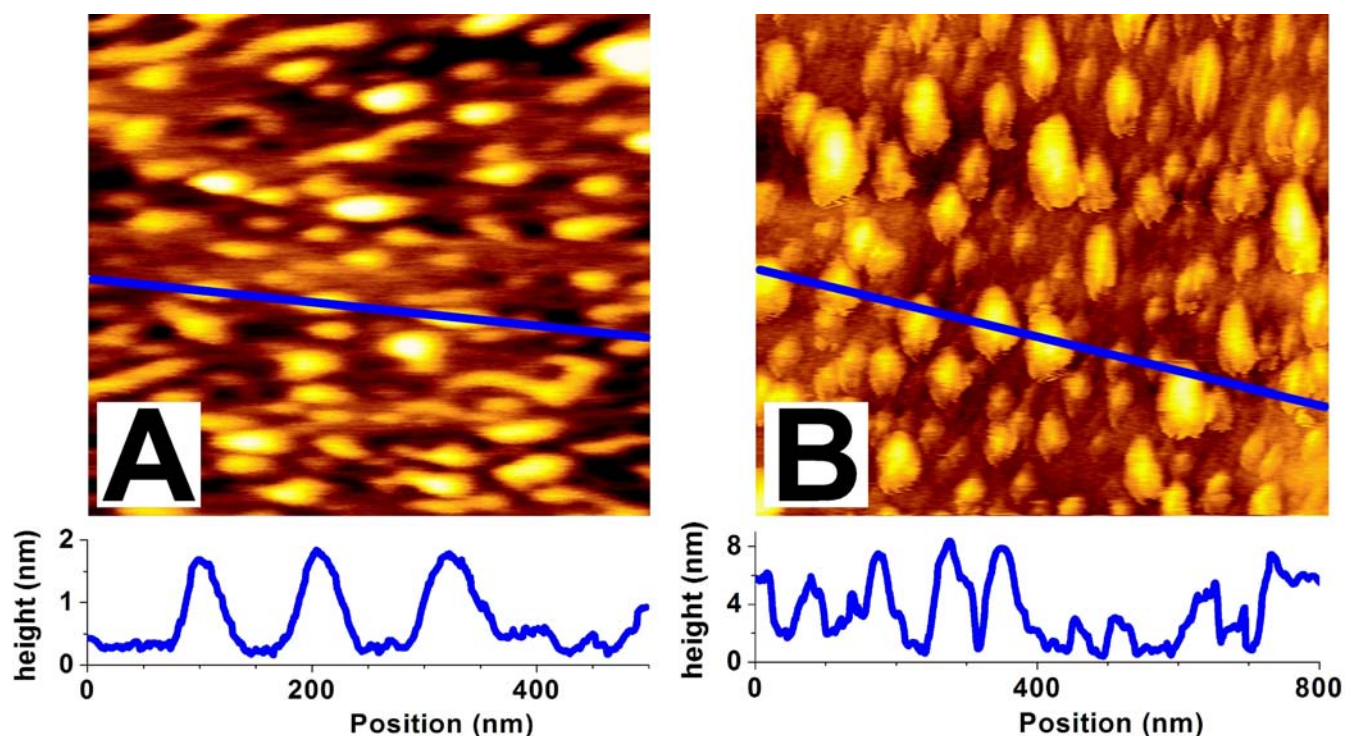


Figure S2 A) AFM topograph and cross-section of a SAM sample that was immersed for 16 hours, 500 nm image width. The image was acquired by using intermittent-contact mode in air with a standard silicon tip. The domain sizes are 30-80 nm. The image is slightly compressed in the vertical direction

because of drift and piezo creep. **B)** AFM intermittent contact mode topograph and cross section of a similar sample in pure water, 800 nm image width. This image was made with a miniature cantilever and nanotube tip. Nanobubbles completely cover the surface. Note the 4 times larger height scale in the cross section and image as compared to **A**).

These bubbles were very stable and could not be moved by imaging with a large interaction force. In some cases, it was possible to either deform or punch through the bubble at its highest point when the amplitude setpoint was decreased (larger interaction force). This deformation was completely reversible.

Another set of samples was incubated for a longer time (approximately 40 hours). This resulted in a distribution of molecules in smaller domains, 10-50 nm, and a higher relative surface coverage of dodecanethiol. Topographs of such a sample are presented in Figure S3. The effect of immersion time on the surface morphology of this SAM system was investigated by Phong et al¹¹. They saw an effect only at total solution thiol concentrations of less than 3×10^{-4} M, where domain sizes grew with time, as can be expected. For concentrations of 1×10^{-3} M, as used here, they find that the surface morphology is determined by absorption kinetics in the first few seconds of incubation and stable for at least 8 days. It is therefore unlikely that the immersion time was the determining factor for the difference in domain size. A possible explanation is a difference in the temperature of the thiol solution at the time of immersion. However, this temperature was not recorded. No noticeable difference was found in the morphology of the gold films used as substrates, and all other procedures followed in making the samples were the same.

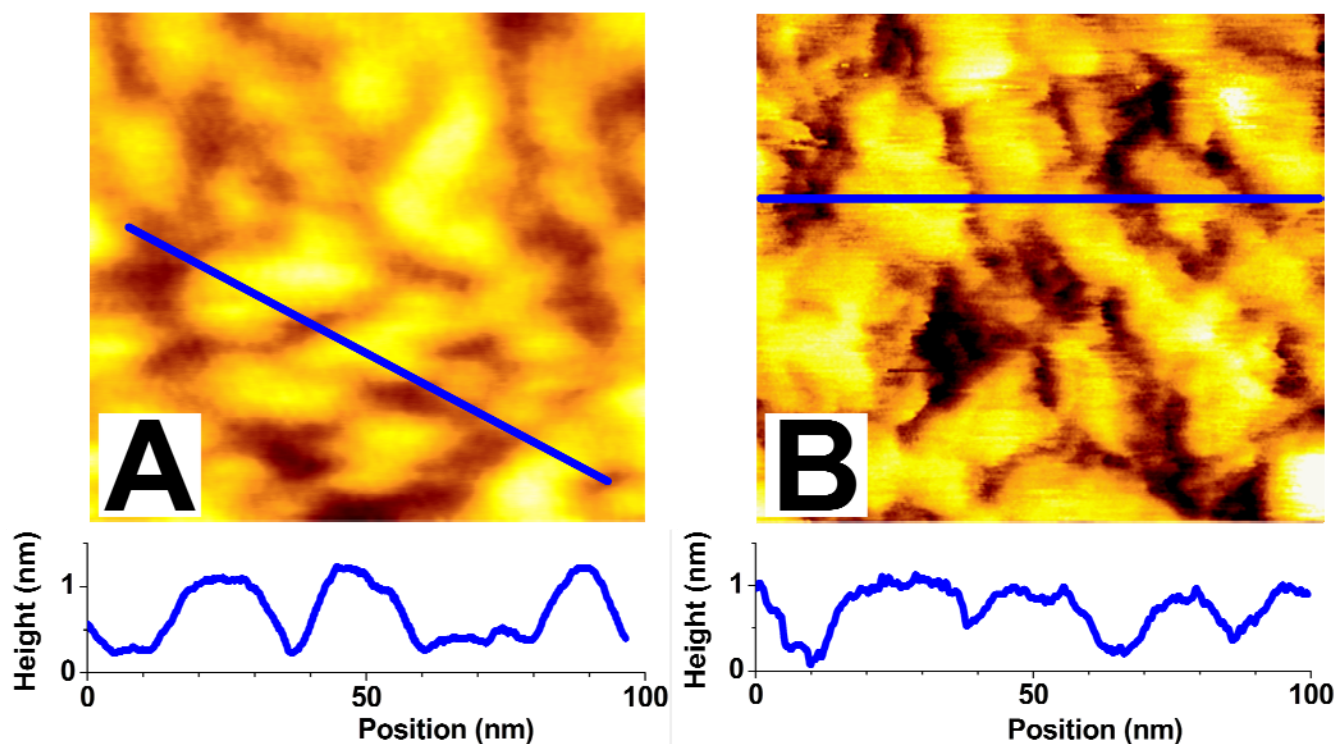


Figure S3 A) AFM topograph and cross section of a SAM sample that was immersed for 40 hours, 100 nm image width. The image was acquired by using intermittent-contact mode in air with a standard silicon tip. The domain sizes are 10-50 nm. This image was smoothed to remove the influence of an external noise source **B)** Topography and cross-section of the same surface as in A), under pure water, 100 nm image width. This image was measured with a miniature cantilever and nanotube tip. A 2nm high ‘nanobubble’ is visible in the bottom right corner of the image, and two smaller ‘bubbles’ can also be distinguished. The smallest hydrophilic gaps between hydrophobic domains seem less deep because of tip convolution.

The samples with smaller domains showed almost no nanobubble formation. A few bubble-like features were seen, but they were significantly smaller and could be removed with repetitive scanning at low amplitude setpoint values. This type of sample was used for force-volume measurements described in the paper.

Self-consistency of force reconstruction from dynamic force-distance curves

In Figure S4 we show the results of numerical experiments which confirm the self consistency of our numerical procedures.

We have approximated the force profile which results from our experiment with a fit function. The fit function was used as the input force profile to calculate the motion of a cantilever (with resonance frequency, Q factor and spring constant as the one in the actual experiment) including thermal noise. This resulted in a noisy ‘numerical measurement’ of amplitude and phase of the cantilever, which can be used to calculate a force profile with our force inversion formula. To reduce the noise in the force inversion we have first fit a smooth function to the ‘numerically measured data’, and subsequently did the force inversion on the smooth function. This resulted in the ‘output force profile’. The small discrepancies between the input and output force profile are smaller than the noise in our experiment and can be ascribed to the small differences between the ‘smooth function’ and ‘the numerically measured data’.

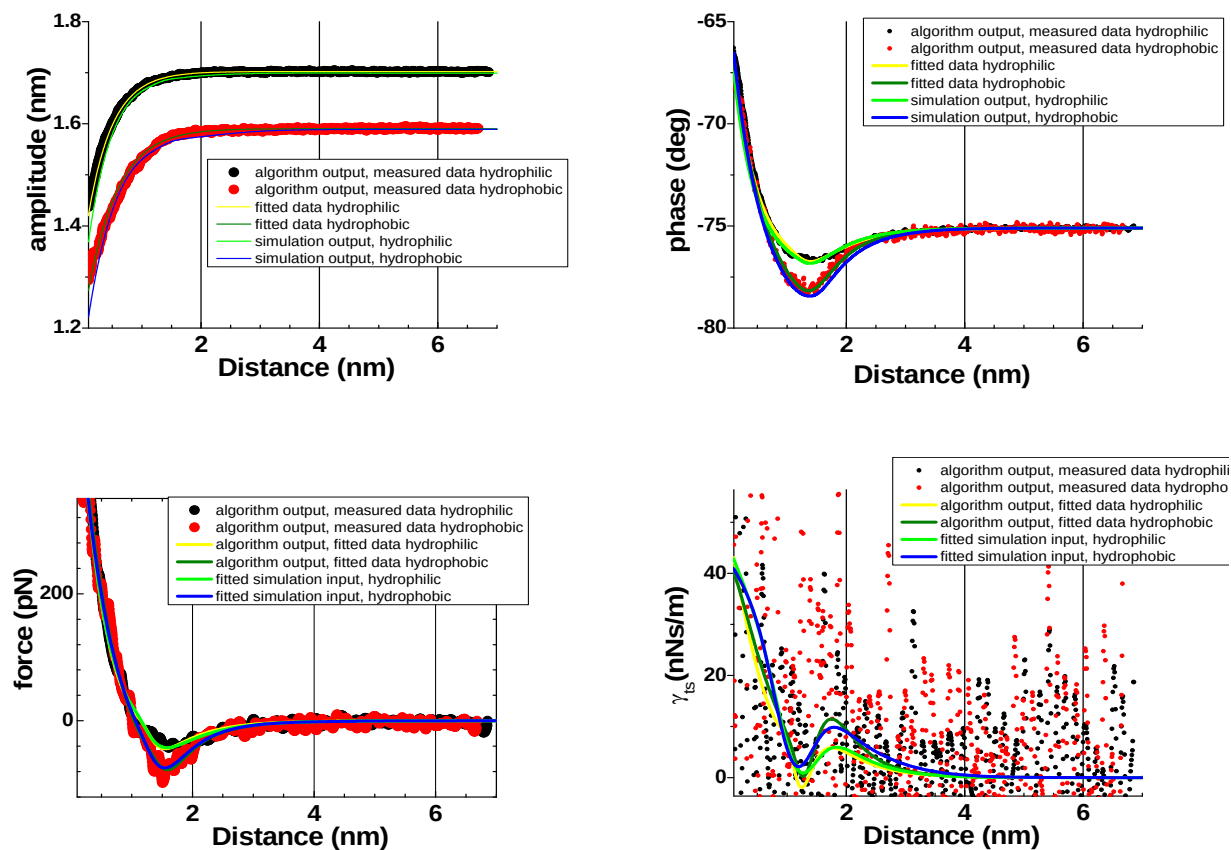


Figure S4. Top: amplitude (left) and phase profiles as measured, fitted and as calculated from measured force profiles. Bottom: Force (left) and damping profiles as calculated from measured data, fits to measured data and calculated forces and damping profiles from numerical simulations with fitted profiles. Fit models and parameters can be found in table S1.

Table S1. Models used to fit force, damping, amplitude and phase profiles presented in figure S4

$$F(z) = -e^{-\left(\frac{w_0}{z}\right)^8} e^{-\frac{z-z_1}{\lambda_0}} + A_0 \left(1 - e^{-\left(\frac{w_0}{z}\right)^8}\right) \left(-1 + A_1 e^{-\frac{z}{\lambda_1}}\right)$$

$$\gamma_{ts}(z) = A_2 e^{-\left(\frac{z+z_3}{w_1}\right)^2} + A_3 e^{-\left(\frac{z+z_4}{w_2}\right)^2}$$

$$a(z) = a_{free} \left(1 + A_4 e^{-\frac{z}{\lambda_2}} + A_5 e^{-\frac{z}{\lambda_3}}\right)$$

$$\varphi(z) = -e^{-\left(\frac{w_3}{z}\right)^5} e^{-\frac{z-z_5}{\lambda_4}} + A_6 \left(1 - e^{-\left(\frac{w_3}{z}\right)^8}\right) \left(-1 + A_7 e^{-\frac{z}{\lambda_5}}\right)$$

	hydrophobic	hydrophilic	
w_0	1.6	1.4	$*10^{-9}$
z_1	-12.2	-13.25	$*10^{-9}$
λ_0	0.59	0.626	$*10^{-9}$
A_0	1.30	0.400	$*10^{-10}$
A_1	6.2	21	$*1$
λ_1	5.7	3.8	$*10^{-10}$

A_2	5.5	7.9	$*10^{-8}$
A_3	-1.9	-1.5	$*10^{-8}$
z_3	-3.8	-7	$*10^{-10}$
w_1	2.4	2.3	$*10^{-9}$
z_4	-1.1	-1.15	$*10^{-9}$
w_2	4.5	4.5	$*10^{-10}$

a_{free}	1.59	1.7	$*10^{-9}$
λ_2	3.3	4.1	$*10^{-10}$
A_4	0.08	-0.21	$*1$
λ_3	4.6	—	$*10^{-10}$
A_5	-0.32	—	$*1$

w_3	1.6	1.4	$*10^{-9}$
z_5	6.0	8.5	$*10^{-10}$
λ_4	5.0	6.5	$*10^{-10}$
A_6	8.0	3.4	$*10^{-2}$
A_7	3.3	6.5	$*1$
λ_5	5.5	4.1	$*10^{-10}$

References

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