Supplemental materials of the article: Force spectroscopy revealed a high gas density state near the graphite substrate inside surface nanobubbles

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Influence of capillary force

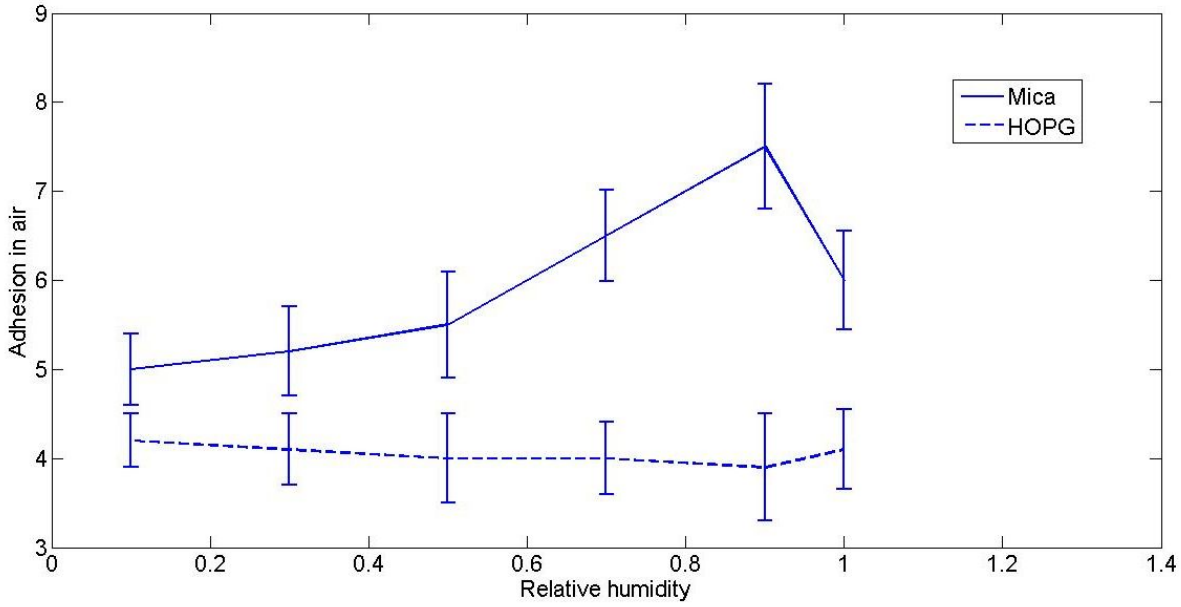
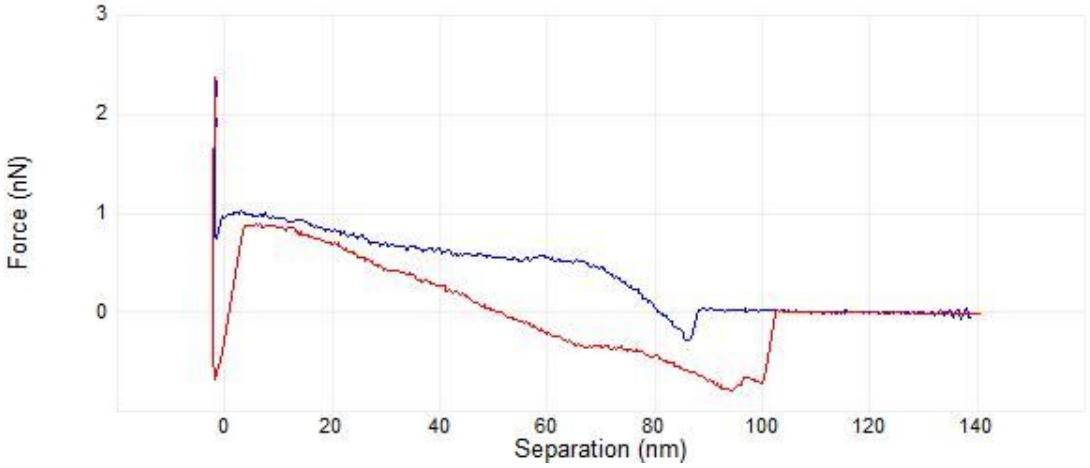


Figure S1. Measured adhesion force as a function of humidity for mica and HOPG against a SiN AFM probe. On mica surface, the adhesion increased by a factor of 50% from 10% to 90% humidity and decreased from 90% to 99% humidity. However, on HOPG surface, the adhesion force is almost independent of humidity. The results were consistent with previous research.[1, 2]

Comparison of force curves on nanodroplets and on nanobubbles

a



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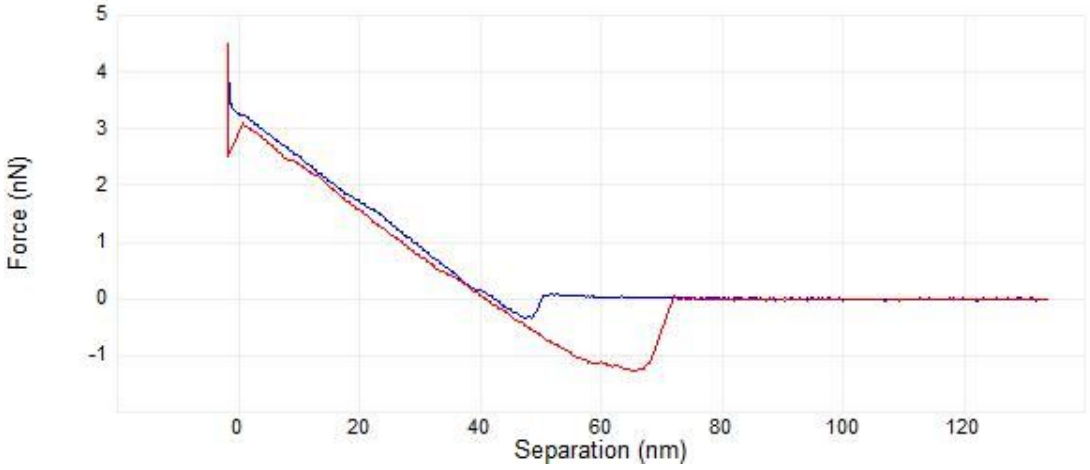


Figure S2. (a) Force curve on nanobubble, (b) force curve on nanodroplet. As the probe contacted with the nanobubble, the three phase line slipped on the probe which showed a nonlinearity and hysteresis region in the curve. This was quite different from force curve on nanodroplet, which a linear region appeared. This difference has been used to distinguish nanobubbles from nanodroplets in some recent works[3, 4].

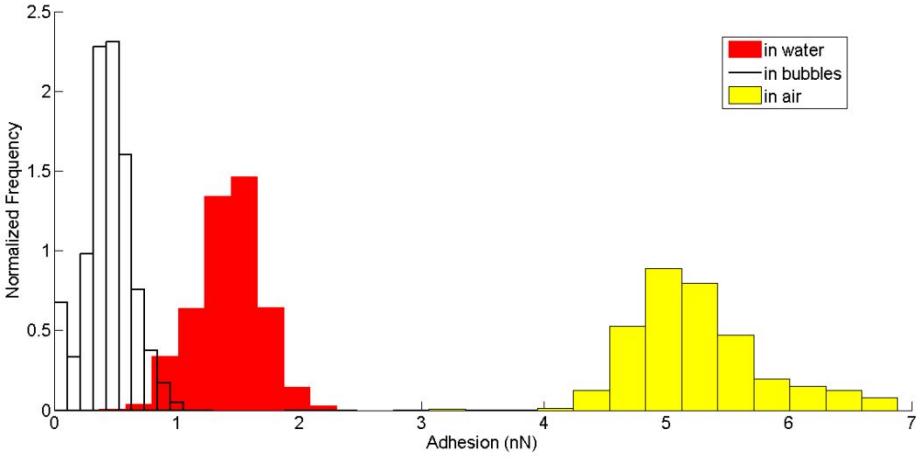
Calculated absolute adhesion compared with experimental values

Table s-1.We could estimate the probe radius by reverse imaging with a polycrystalline titanium sample, which gave radius less than 10 nm, with D in the order 0.2 nm, inserting these values into equation (1). We could calculate the adhesion in different conditions, given in the table below

	Hamaker constants (J)	Calculated adhesion (nN)	Measured adhesion (nN)
Graphite in air	2.45e-19	10.2	5.3
Graphite in water	1.20e-19	5	1.6

Adhesion inside nanodroplets

a



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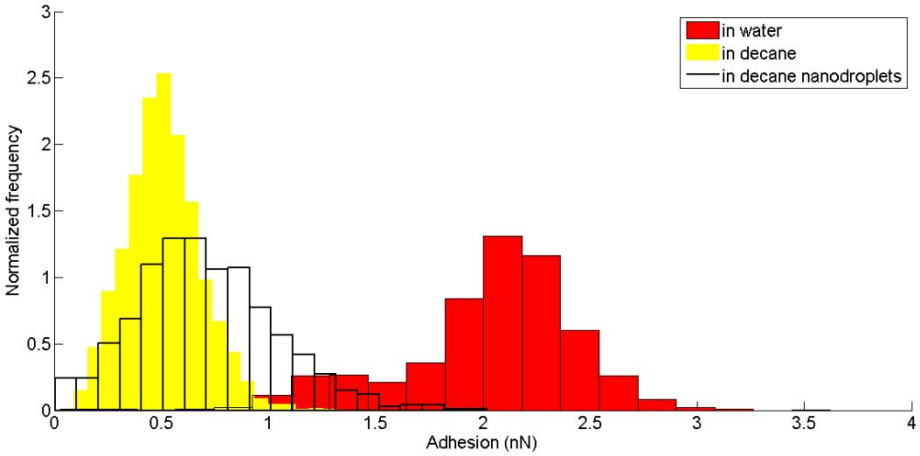


Figure S3. Histograms of adhesion inside nanobubbles and nanodroplets. (a) Histograms of adhesion, patch with black lines, adhesion inside nanobubbles, patch with red face, adhesion in water, patch with yellow face, adhesion in air (99% humidity). The adhesion in air is much larger than inside bubble. (b) The control experiment performed on decane nanodroplets, patch with black lines, adhesion inside decane nanodroplets, patch with red face, adhesion in water, patch with yellow face adhesion in pure decane. It should be noted that the adhesion in decane nanodroplet was approximately the same in pure decane. We calculated the adhesion in these systems using Lifshitz theory of van der Waals force,

$$\frac{F_{water}}{F_{air}} \sim \frac{1}{2}$$

$$\frac{F_{water}}{F_{decane}} \sim \frac{6}{5}$$

The results were consistent with our experimental observation.

Numbers of nitrogen molecules inside bubble as a function of time

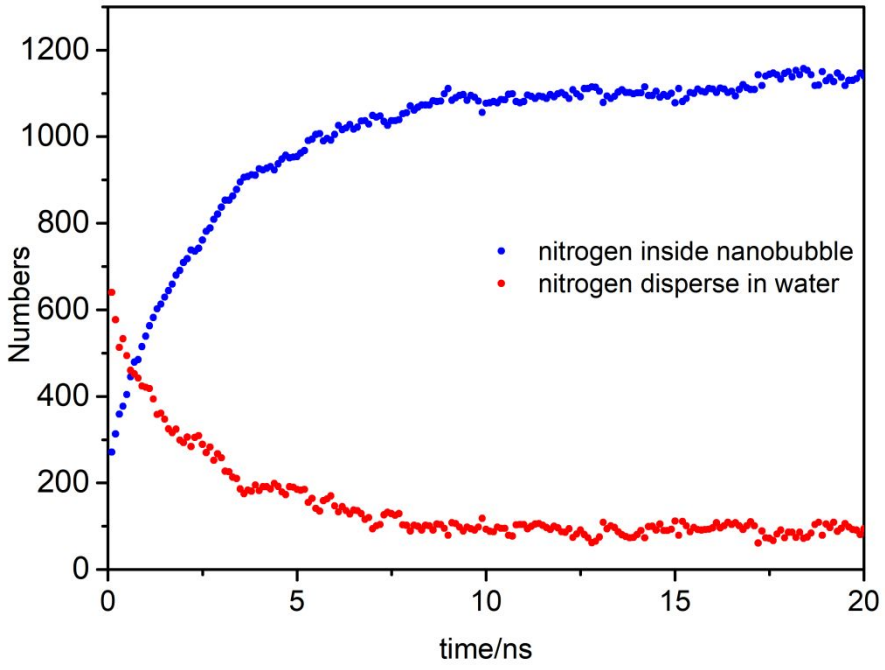


Figure S4. Numbers of nitrogen molecules inside the spherical cap nanobubble and dispersed in water as a function of simulation time. Only the top half of the simulation box was considered. This result suggested that the system has reached equilibrium at about 10ns.

Distribution of water molecules inside the simulation box

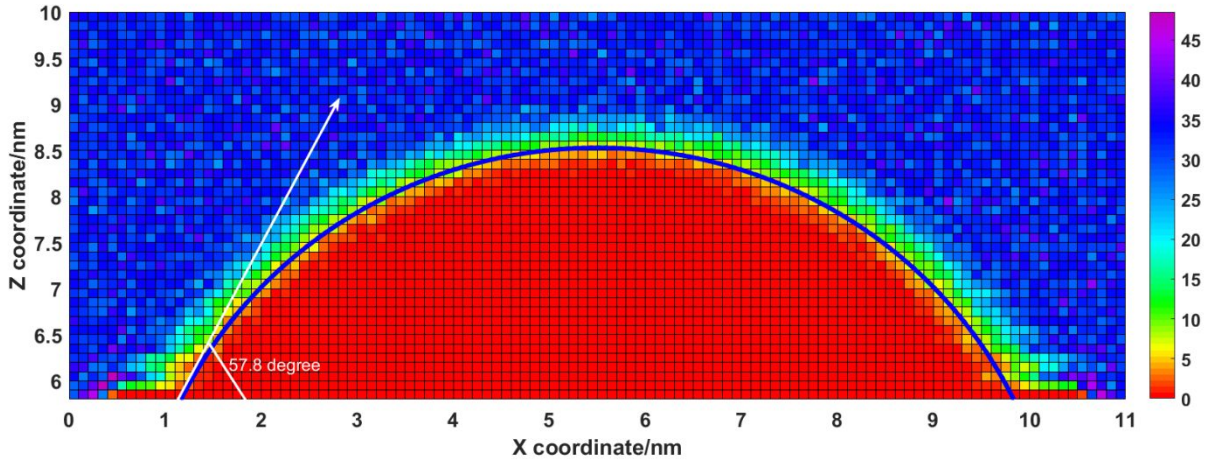
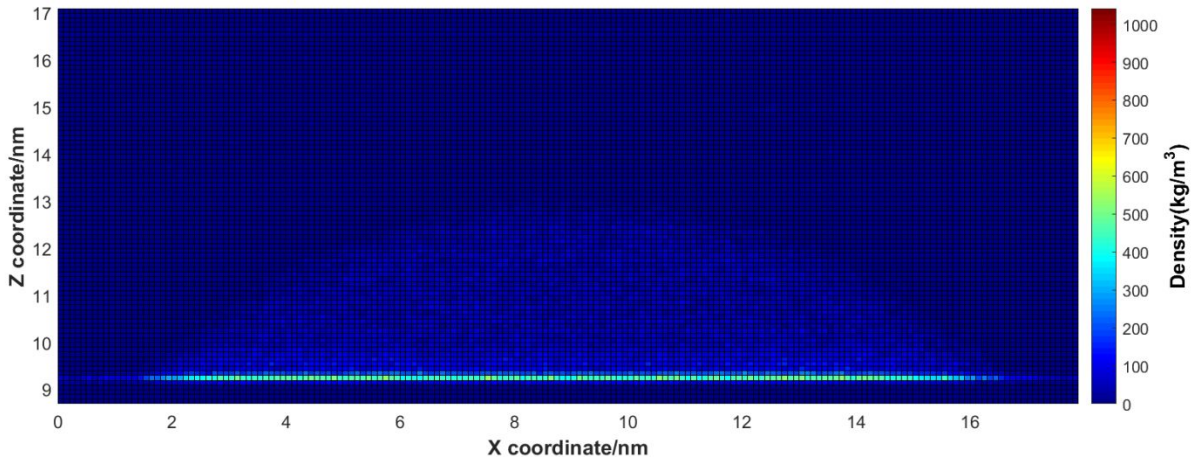


Figure S5. Average number density of water molecules around the nitrogen nanobubble in the x-z plane. Notice that the average number density of water molecule at 300K is about 33 per nm^3 (marked as Bulk density). The liquid/gas interface was determined by finding the cubic square density lies in [0.05~0.1] *Bulk density. Then the liquid/gas interface was fitted by circular arc with minimal deviation. Notice that same procedure using y-z plane yield similar results.

Size dependent density in MD simulations

a



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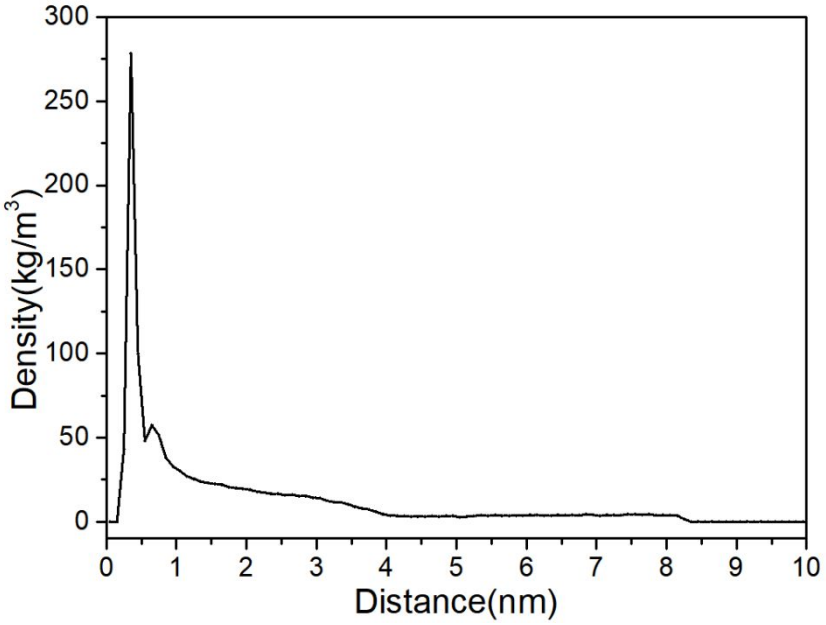


Figure s6. MD simulation results for a larger bubble. (19 nm) a) the nitrogen density distribution in the simulation box, b) the density distribution as a function of distance to the substrate. The features were very similar to the results reported in the main article, with lower density.

Influence of the inhomogeneous dense layer on the adhesion force

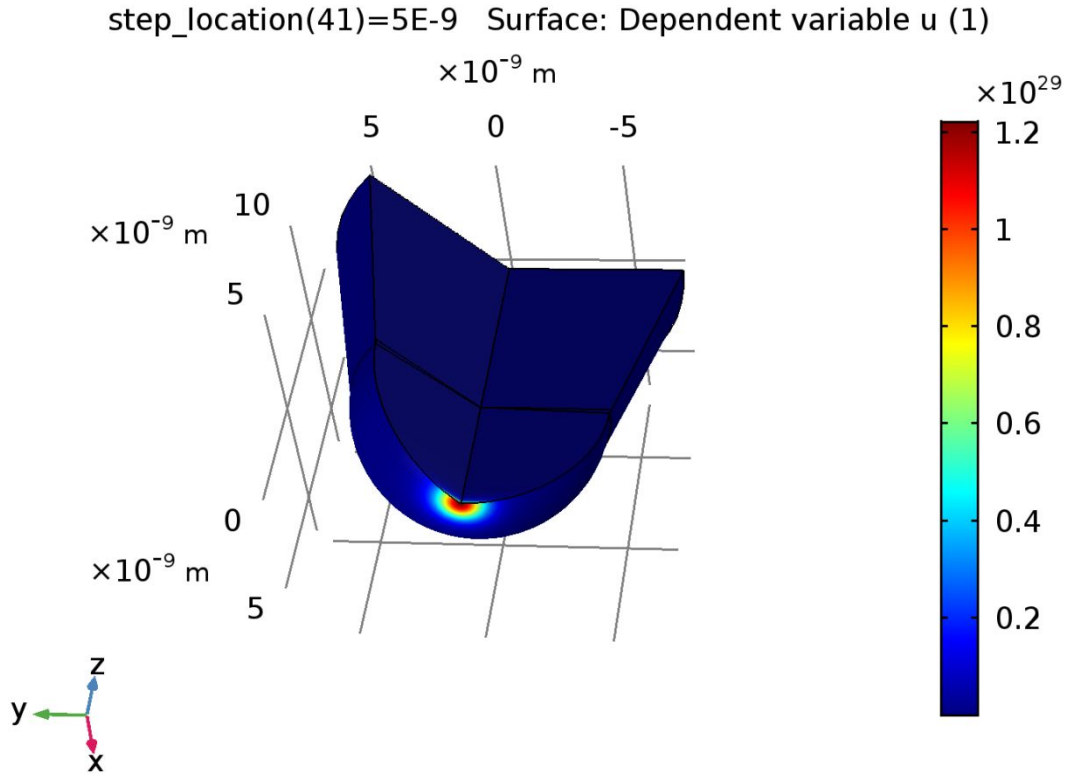


Figure s7 Calculated force density (N/m^3) distribution in the probe. The force mainly distributed in the apex region.

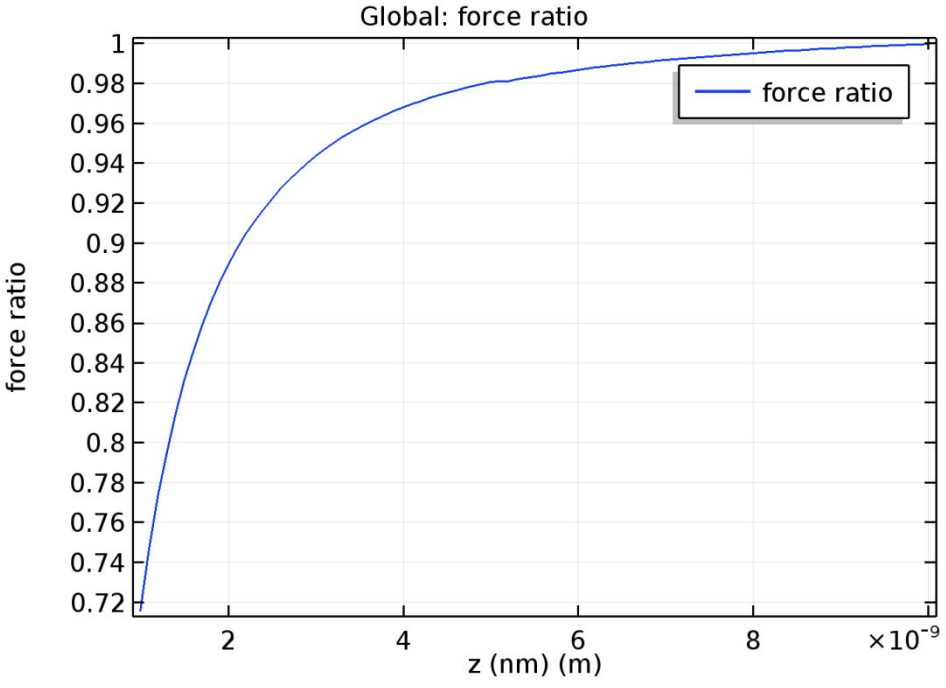


Figure s8. The integrated force along z direction. 90% of the force distributed under 2 nm, medium above this region did not affect much about the adhesion. The adhesion is only sensitive to the environment near the interface.

Influence of contact time on the adhesion force

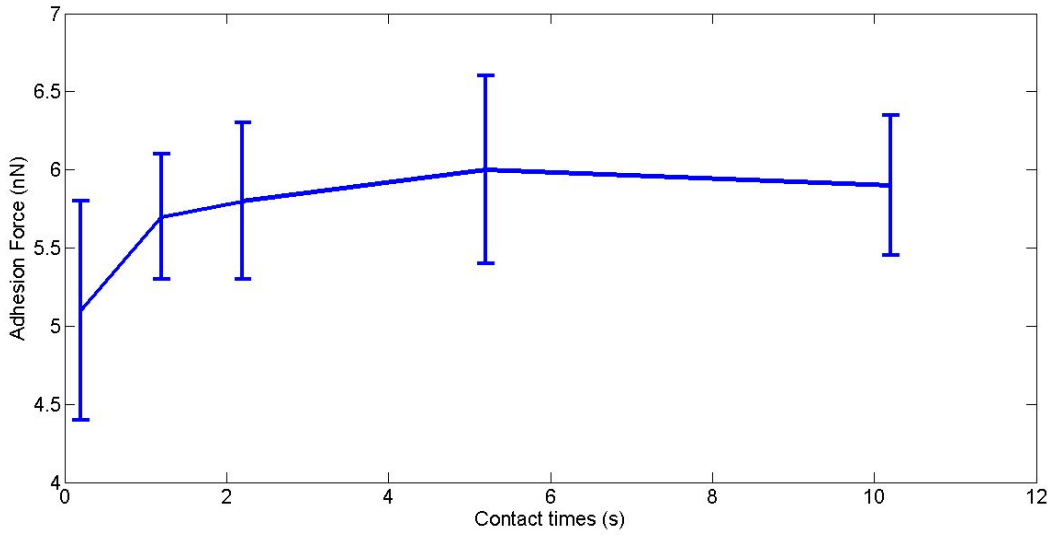
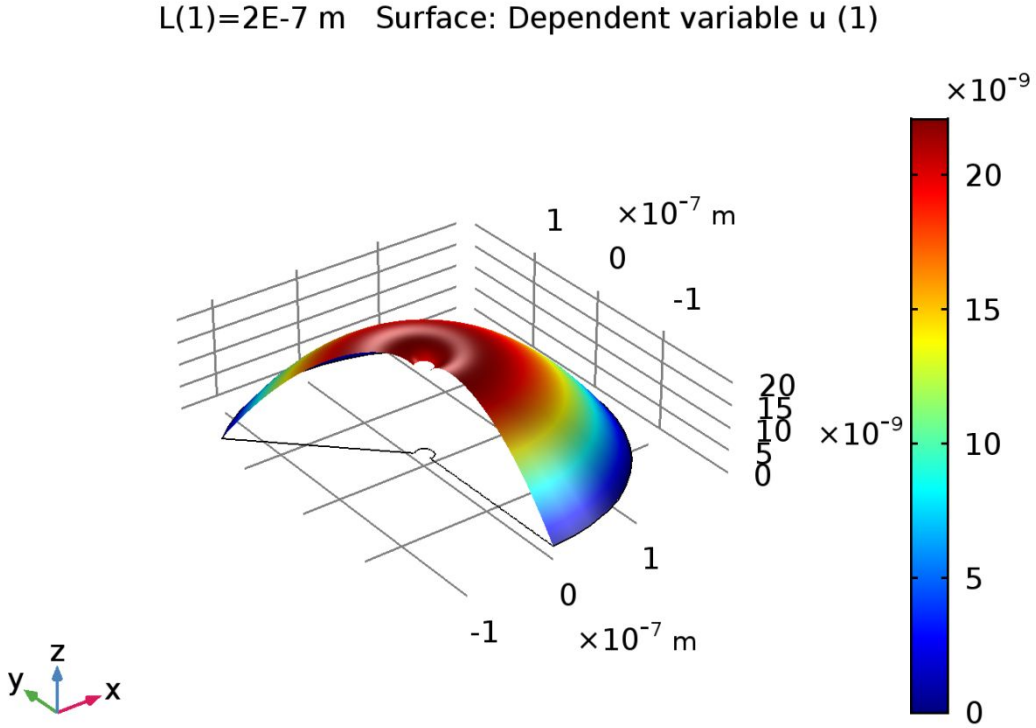


Figure s9 Measured adhesion force on HOPG surface as a function of contact time.

Influence of the normal force on the shape of nanobubbles

A



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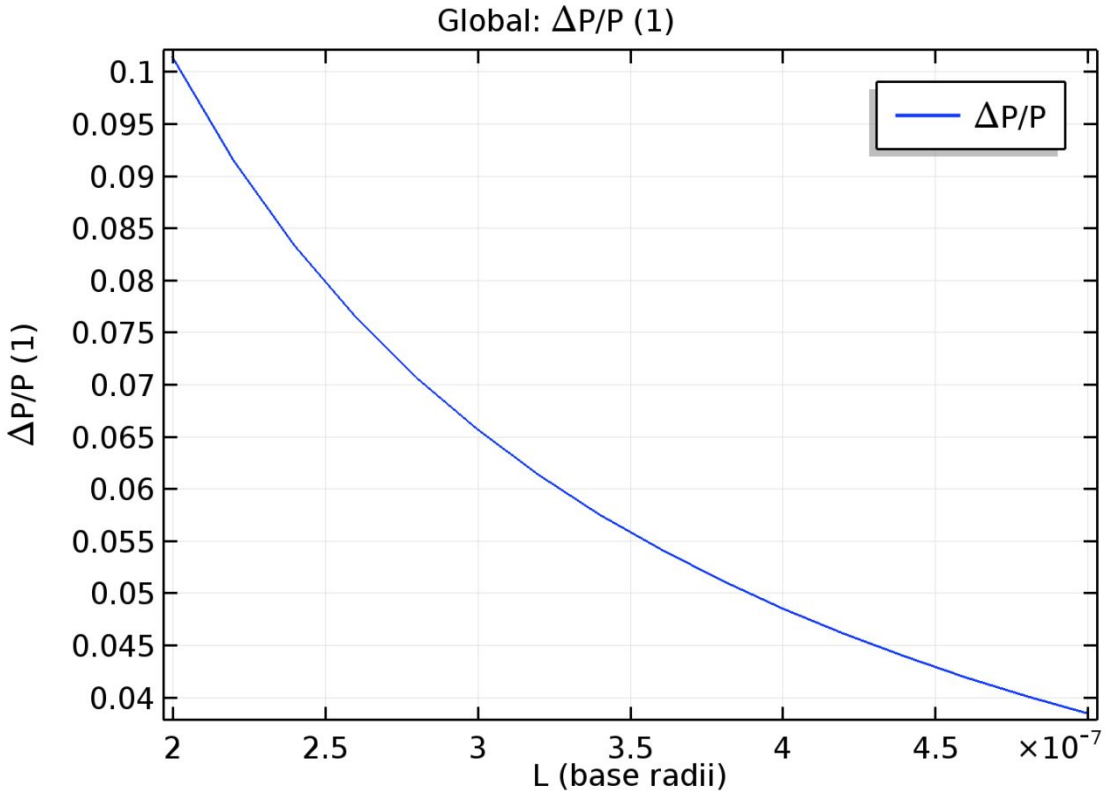
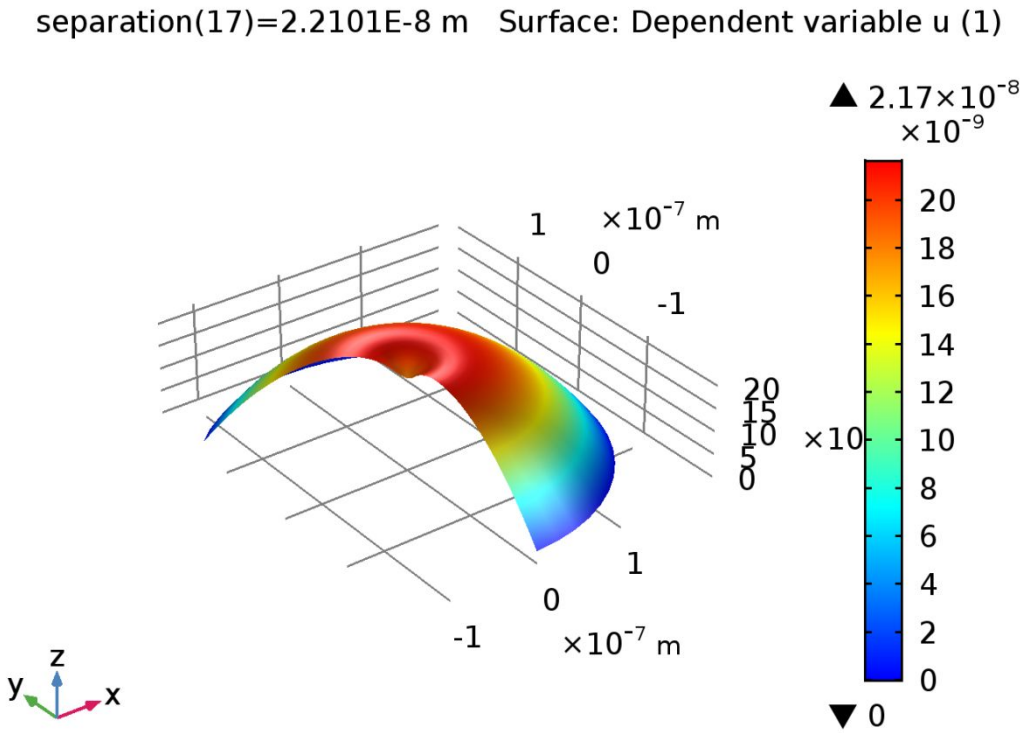


Figure s10. The profiles of nanobubbles under application of forces. (a) The Calculated profile of the air/water interface of a bubble (base radius 200 nm) approached by an AFM probe with 1 nN normal force. (b) The relative changes of the Laplace pressure $\Delta P / P$ as a function of bubble size, note that changes is below 10% for bubbles larger than 200 nm.

Force curves in SDS solution

a



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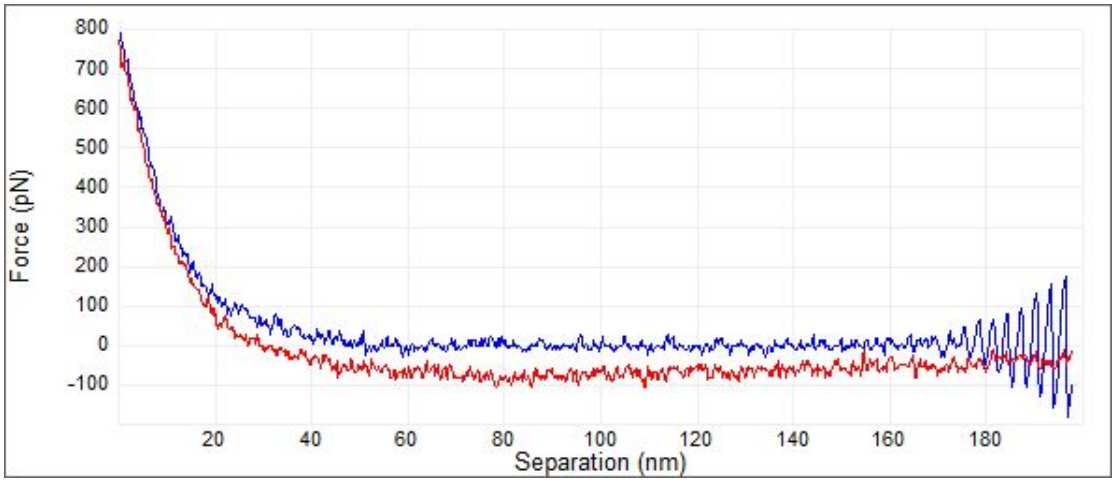

Figure. S11. Forces curves in 10 mM SDS solution. (a) Calculated profile of the air/water interface of a bubble approached by an AFM probe, in 10 mM SDS solution, in this case, the probe did not penetrate into the bubble, the air/water interface deformed to a dimple at the top (b) Measured force curves on a nanobubble in 10 mM SDS solution, note that there was no snap-in as the probe approaching to the bubble.

The detail process of the probe proceed in the nanobubble

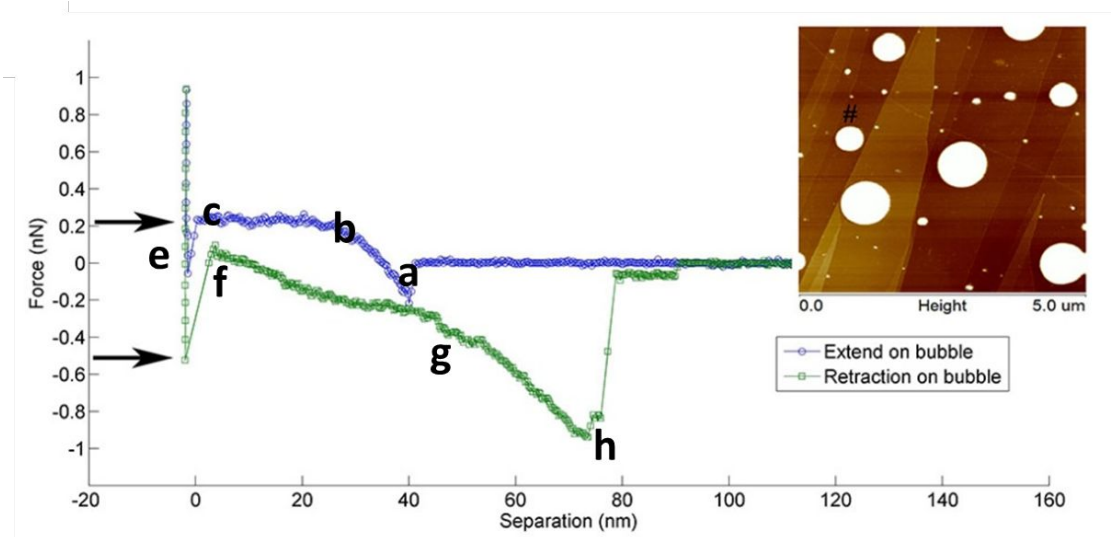

Figure s12. The detail process of the probe proceed in the nanobubble. The probe first snapped into contact with the bubble at a separation of 40 nm, from a to b the three phase line was pinned on the probe, from b to c, the three phase line started to slip, and snapped into contact with the substrate. As the motion reversed, the probe first jumped off contact with the substrate, from f to g, the three phase line slipped on the probe with a different contact angle, from g to h, the contact line pinned, finally the probe jumped off contact with the bubble at h. The response was linear in two pinning region, a to b and g to h. We cannot deduce the exact contact angle during the slip region, due to the lack of the accurate shape information of the probe. However, the hysteresis in the force curve was mainly caused by the contact angle hysteresis in the slip region.

1. Farshchi-Tabrizi, M.; Kappl, M.; Cheng, Y.; Gutmann, J.; Butt, H.-J. On the Adhesion between Fine Particles and Nanocontacts: An Atomic Force Microscope Study. *Langmuir* 2006, *22* (5), 2171-2184.

2. Xiao, X.; Qian, L. Investigation of Humidity-Dependent Capillary Force. *Langmuir* 2000, *16* (21), 8153-8158.

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4. Wang, X.; Zhao, B.; Hu, J.; Wang, S.; Tai, R.; Gao, X.; Zhang, L. Interfacial gas nanobubbles or oil nanodroplets? *Physical Chemistry Chemical Physics* 2017, *19* (2), 1108-1114.