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Nanobubbles Do Not Sit Alone at the Solid-Liquid Interface

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Abstract

The unexpected stability and anomalous contact angle of gaseous nanobubbles at the hydrophobic solid-liquid interface has been an issue of debate for almost two decades. In this work silicon-nitride tipped AFM cantilevers are used to probe the HOPG-water interface with and without solvent-exchange (a common nanobubble production method). Without solvent-exchange the force obtained by the single force and force mapping techniques is consistent over the HOPG atomic layers and described by DLVO theory (strong EDL repulsion). With solvent-exchange the force is non-DLVO (no EDL repulsion) and the range of the attractive jump-in (>10 nm) over the surface is grouped into circular areas of longer range, consistent with nanobubbles, and the area of shorter range. The non-DLVO nature of the area between nanobubbles suggests that the interaction is no longer between a silicon-nitride tip and HOPG. Interfacial gas enrichment (IGE) covering the entire area between nanobubbles is suggested to be responsible for the non-DLVO forces. The absence of EDL repulsion suggests that both IGE and nanobubbles are not charged. The co-existence of nanobubbles and IGE provides further evidence of nanobubble stability by dynamic equilibrium. The IGE cannot be removed by contact mode scanning of a cantilever tip in pure water, but in a surfactant (SDS) solution the mechanical action of the tip and the chemical action of the surfactant molecules can successfully remove the enrichment. Strong EDL repulsion between the tip and nanobubbles/IGE in surfactant solutions is due to the polar heads of the adsorbed surfactant molecules.

1 Introduction

The existence of gaseous nanobubbles accumulated at the hydrophobic solid-liquid interface has been a topic of intense debate since nanobubbles were hypothesized to explain steps and variability in force data measured between hydrophobic surfaces in water¹. Mounting experimental evidence demonstrates that interfacial nanobubbles (here to referred to as nanobubbles) do exist at the hydrophobic solid-liquid interface under certain conditions²⁻¹². Despite extensive experimental and theoretical endeavor devoted to nanobubbles, a comprehensive understanding of the anomalous stability and contact angle is still an active area of debate¹²⁻¹⁷.

Proposed mechanisms for surface nanobubble stability include contamination¹³, dynamic equilibrium¹⁴ and contact line pinning¹⁸⁻²⁰. The disappearance of nanobubbles by exposure to surfactants above the critical micelle concentration (cmc) leads researchers to suggest that stabilization of nanobubbles in water is due to a film of insoluble contaminants at the air-water interface, which is removed by the micelles¹³. However, Zhang et al.²¹ recently demonstrated nanobubbles do exist in micellar solutions but are just very difficult to image by tapping mode. Thus, contamination is not responsible for the stability of nanobubbles. In the dynamic equilibrium model outgoing gas molecules from gas-liquid interface are balanced by influx near the three phase contact line, resulting in a metastable equilibrium¹⁴. The influx at the contact line is believed to be feed by gas enrichment at the solid-liquid interface, with evidence of such interfacial gaseous enrichment (IGE) provided by molecular dynamics simulations^{17, 22, 23}, recent AFM experiments reporting the growth of molecular layer gas-like domains at the HOPG-water interface²⁴ and the co-existence of nanobubbles and micro-pancakes^{5, 11, 25-29}.

The existence of an IGE has been hypothesized by van Limbeek⁷ and Weijs¹⁷ as the reason for the anomalous contact angle and stability of nanobubbles. If an IGE co-exists with nanobubbles then the Young equation for contact angle cannot be determined simply by the surface

free energies of the HOPG-water, water-vapor and HOPG-vapor. The role that an IGE plays in the thermodynamics of wetting at the nanoscale may explain the anomalously high contact angle of nanobubbles. Based on our molecular simulation results for this new system (to be published) the contact angle (gas side) is around 20° , which is in range of the reported values³⁰⁻³². In the recent report by Limbeek and Seddon⁷ the contact angle of nanobubble was found to be significantly affected by gas type compared to solid type. They conclude that these phenomena result from nanobubbles sitting on top of adsorbed gas molecules.

The dynamic equilibrium model and IGE leads us to a new question regarding studies undertaken using the proven nanobubble producing method of solvent-exchange³³⁻³⁵. It is clearly demonstrated that a process such as solvent-exchange is necessary to form nanobubbles at a surface such as HOPG. However, does solvent-exchange also result in IGE between the nanobubbles? To answer this question an AFM force spectroscopy study investigating the effect of solvent-exchange on the interaction between HOPG and a silicon-nitride (Si_3N_4) tip in water was undertaken. If solvent-exchange does produce IGE in the area surrounding nanobubbles it is hypothesized that the force measured in this area will be different to that experienced in a “clean” Si_3N_4 /HOPG/water system never exposed to solvent-exchange. Additionally, the interaction of nanobubbles/IGE with soluble surfactant are investigated as such a system will provide additional detail and nanobubbles/IGE and is of importance in applications such as froth flotation and particle processing.

2 Methods

2.1 Materials Preparation

Sodium dodecyl sulfate (SDS) was purchased from Sigma-Aldrich (Australia) and purified by re-crystallization in ethanol. Highly Ordered Pyrolytic Graphite (HOPG, ZYB grade) was obtained from SPI Supplies (West Chester, USA) and freshly cleaved to produce a clean surface. The advancing contact angle of water droplets on the HOPG surface is about 80° as measured by a

PAT1 tensiometer (SInterface, Germany). AR grade ethanol was obtained from Crown Scientific (Australia). Water was freshly purified using a setup consisting of a reverse osmosis RIO's unit and an Ultrapure Academic Milli-Q system (Millipore, USA). Since contamination would be one of the mechanisms of nanobubble formation and stability, significant effort was focused on keeping contamination to as acceptably low as possible by using high purity chemicals, effective cleaning procedures for cantilevers and glassware and consistent methodical handling of the substrates and AFM fluid cell. Specifically, the consistency of the silicon nitride-HOPG force curves in water before solvent exchange is attest to contamination reduction procedures used in this work. Additionally, the surface tension measurements of the ethanol before and after foam fraction by bubbling with nitrogen for one hour also showed no changes in surface tension.

2.2 Measurement Methods

Atomic Force Microscope (AFM) force spectroscopy was completed with a Nanoscope IV (Veeco, Santa Barbara, USA) AFM using the contact mode fluid cell. NP Si₃N₄ tipped triangular cantilevers (Veeco, Santa Barbara, USA) with nominal spring constant of 0.06-0.12 N/m (actual spring constant determined by resonance frequency³⁶) were used. The cantilevers were cleaned with acid-piranha treatment, washed with Milli-Q water and exposed to UV light (254 nm wavelength) for 30 min before use. The piranha solution consisted of a mixture of 98% concentrated H₂SO₄ and 30% hydrogen peroxide in a 3:1 volumetric ratio. Single force measurements were performed at scan rates at 1 μm/s while force maps (64 lines and 64 force curves per line) were performed at 5 μm/s. The AFM setup was allowed to settle for at least 30 min to minimize thermal drift before starting the actual force measurements. The scan size was varied between 5 μm × 5 μm and 10 μm × 10 μm to ensure that a sufficient number of nanobubbles were present in each of the force maps. Additionally, the size of the scans was much larger than the thermal drift, rendering the effect of thermal drift as minimal. The nanobubbles were formed using the well-known solvent-exchange method where ethanol is first introduced into the AFM cell followed by four successive 5 mL

injections of Milli-Q water. The effect pumping on the nanobubble formation and stability was minimized by using small speed (0.5 mL per hour) of the syringe pump for both the ethanol and SDS solution injections. All measurements were performed at a temperature of $23 \pm 2^\circ\text{C}$. Force curves were processed using SPIP 6.0.2 (Image Metrology, Denmark) and force mapping analysis carried out using the Nanoscope 5.3 software (Veeco, Santa Barbara, USA).

3 Results and Discussion

3.1 *Effect of Solvent Exchange on Surface Forces*

The DLVO nature of the force between a Si_3N_4 tip and the HOPG surface in water without solvent exchange is shown in Figure 1a. The force at separations distances > 5 nm is characterized by the repulsive electrostatic double layer (EDL) force as shown by the linearity of a semi-log force vs. separation plot. A repulsive EDL was expected as the interacting surfaces both have negative surface potential in pure water ($\text{pH} = 5.6$), with HOPG at approximately -22 mV^{37} and a weak negative potential for Si_3N_4 (isoelectric point at $\text{pH} 5\text{-}6^{38}$). The HOPG surface is negatively charged due to the lone pair of delocalized electrons of the C_6 rings³⁹. The slope of the data correlates well with a background electrolyte concentration of 0.1 mM (i.e. Debye length of 30.3 nm). Below 5 nm an attractive force with jump-in to contact is due to the van der Waals (vdW) force. The force is reproducible over the HOPG atomic layers and between experiments. After solvent-exchange the force between a Si_3N_4 tip and the HOPG surface in water can no longer be explained by DLVO, as shown in Figure 1b. A long-range (>10 nm) non-DLVO attractive force occurs with a significant variability in range between experiments and between different locations within the same experiment. No measurable EDL force could be detected at any point on the surface after solvent-exchange.

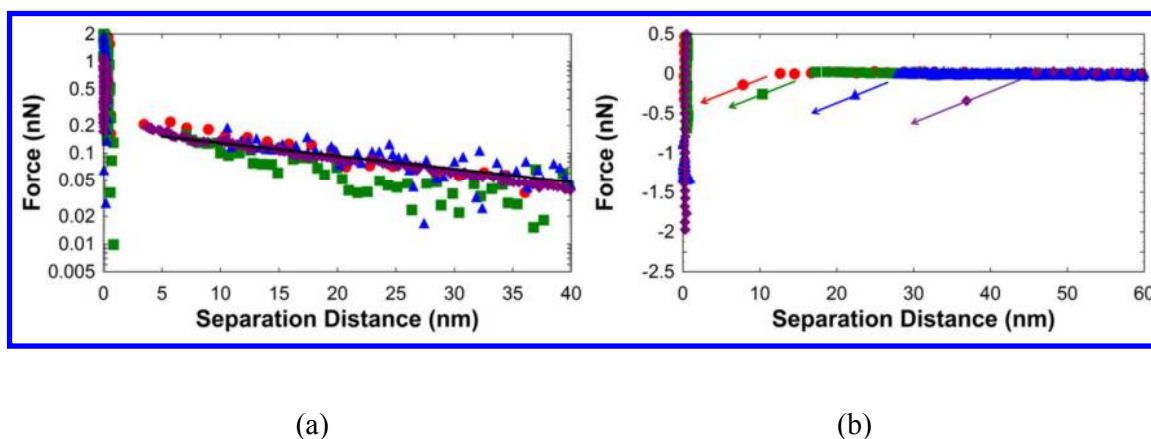


Figure 1: Force curves of between a Si_3N_4 tip and HOPG in a) water without solvent-exchange and b) in water after solvent-exchange. Four sets of data from different experiments are shown in each case to show the reproducibility of the force without solvent-exchange and the variability after solvent exchange. The black line in (a) is an exponential fit to the data with a Debye length of 30.3 nm (≈ 0.1 mM background electrolyte).

A long-range attractive force of variable range after solvent-exchange was expected due to the formation of nanobubbles on the surface^{30, 40}. As nanobubbles are found to cover only a certain portion of the HOPG surface^{4, 9, 27, 30} it was anticipated that some of the force curves would resemble that of a Si_3N_4 interacting with a pristine HOPG surface, like the force curves in water without solvent-exchange (Figure 1a). However, no such force curves were measured despite many different experiments, some of which involved force maps containing a matrix of thousands of force measurements. An example of such a force map indicating the range of the attractive jump-in force is shown in Figure 2 along with a few example force curves at different locations. Similar to the observation by Zhang et al.³⁰, distinct circular areas of long jump-in distances occurred over the surface, which are indicative of nanobubbles (i.e. the darker regions in Figure 2). The two example force curves in a nanobubble-area have jump-in distances of 38 nm and 53 nm, corresponding to a typical nanobubble height^{30, 41}. Non-nanobubble areas do not have such a long range, but the jump-in > 10 nm and the lack of an EDL force proves that the forces are different to the force between a Si_3N_4 tip and a HOPG surface in water without solvent-exchange. It is conclusively demonstrated by these force spectroscopy results that the solvent-exchange process not only creates nanobubbles in certain areas, but changes the HOPG-water interface between

nanobubbles. IGE (as molecular layer gas-like domains and/or micro-pancakes) is proposed as the reason for the non-DLVO forces.

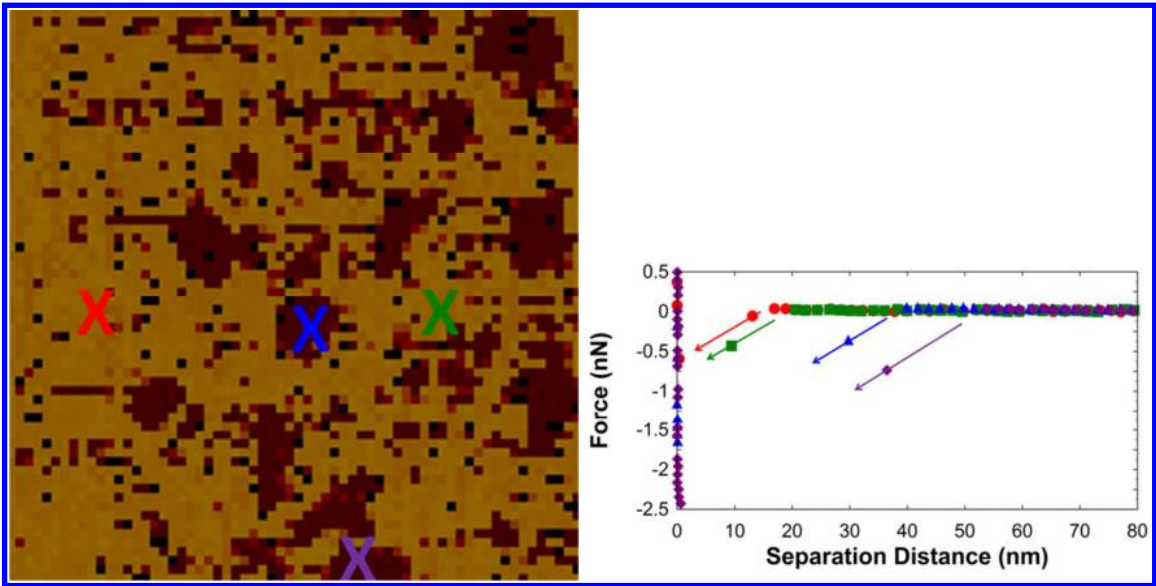
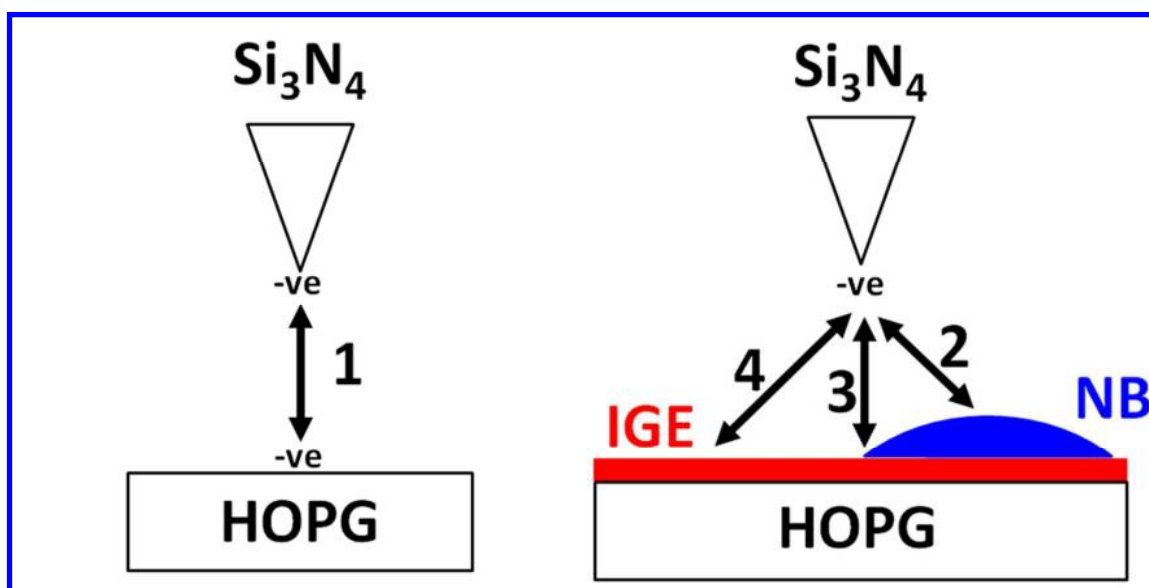


Figure 2: a) 5x5 μm AFM force map indicating jump-in distance (darker color indicates longer jump-in distance) of HOPG in water after solvent-exchange and b) example force curves (the color of the X on the force map corresponds with the color of the force data).

A schematic illustrating how solvent-exchange induced nanobubbles and IGE dramatically change the force is provided in Figure 3. In the case without solvent-exchange (Figure 3a) the interaction occurs between a pristine Si₃N₄ tip and the atomic HOPG layer across pure water and is consistent and well described by DLVO. After solvent-exchange the interaction becomes more complex as the Si₃N₄ tip can interact with nanobubbles of various size, different areas of the same spherical-capped shaped nanobubble and IGE between the nanobubbles, which may consist of patchy molecular layer of gas and/or micro-pancakes. In the case of the interaction with a nanobubble it was expected that before piercing the nanobubble a significant EDL force would be measured, similar to colloidal probe experiments with microbubbles⁴²⁻⁴⁴. The surface potential of a bubble in pure water is experimentally determined to be approximately -65 mV^{42, 45}, while for a

HOPG surface the surface potential is lower in magnitude at approximately -22 mV^{37} . An EDL force is measurable at a HOPG surface (Figure 1a), therefore the cantilevers used have the sensitivity required to measure an EDL force at a nanobubble with a surface potential similar to that of a microscopic bubble. The lack of an observable repulsion on approach to a nanobubble differs to the results of Zhang et al.³⁰ who observes a very weak repulsive force before jump-in for some data. Such a weak repulsion is possibly also present in the experiments undertaken here, but the signal to noise ratio maybe too low. Regardless, the lack of a significant EDL repulsive force demonstrates that the surface potential of a nanobubble is much lower than that of a HOPG surface and hence lower than a microscopic bubble, suggesting a different charging mechanism for a nanobubble. Another difference between the nanobubble interactions shown here and that of Zhang et al.³⁰ is that after penetrating the nanobubble Zhang measures a finite resistance until contact. This finite resistance was also reported by Ishida et al.⁴¹. No such resistance was found in the thousands of force curves taken in this work. At this point the reason for the discrepancy might be related with the use of the cantilevers with low spring constants, meaning that the tip might jump straight into contact without significant deflection due to hydrodynamic resistance which otherwise could happen at high approach speed. However, no such resistance was observable in this work (such a resistance is observed however when surfactant is added to the system as outlined in Section 3.2).



(a)

(b)

Figure 3: An illustration of the interaction between a Si_3N_4 tip and a HOPG surface in water a) without solvent exchange and b) after solvent exchange. Interaction 1 is characterized by repulsive EDL force (both silicon-nitride and HOPG are negatively charged at pH 5.8) and an attractive vdW force (< 10 nm). After solvent exchange three types of forces are possible. Interaction 2 is a Si_3N_4 -nanobubble top force characterized by the longest attractive jump-in to contact and no EDL force.

Interaction 3 is a Si_3N_4 -nanobubble side force characterized by a smaller attractive jump-in to contact and no EDL force. Interaction 4 is a Si_3N_4 -IGE force characterized by an attractive jump-in to contact (>10 nm) with no EDL force. Schemes are not to scale.

An interesting aspect of the recent work of Lu et al.²⁴ on growth of a molecular layer of gas-like domains at the HOPG-water interface is that tapping mode AFM imaging strongly disturbed the layer, but did not remove it. To test if disturbing nanobubbles and the IGE with the Si_3N_4 tip changed the forces a contact mode image was taken multiple times after-solvent exchange over a $5 \times 5 \mu\text{m}$ area and force curves taken within the scanned area. The force curves within the area were the same as the non-DLVO forces outside the scanned area and those presented in Figure 1b and Figure 2. As the forces did not change it would seem that tip perturbation in pure water may have disturbed nanobubbles and IGE, but it did not remove them.

3.2 Effect of Solvent Exchange on SDS Adsorption

Recent works have studied the surfactant effect on nanobubbles^{13, 21, 30}. It was initially thought that sodium dodecyl sulfate (SDS) at a concentration above the critical micelle concentration (cmc) could remove nanobubbles¹³, but actually, SDS just makes it very difficult to image nanobubbles with tapping mode AFM²¹. It is now known nanobubbles can survive in SDS solutions, hence further investigation on the effect of nanobubbles and the IGE on surfactant adsorption is necessary.

The self-assembly of surfactants on a variety of hydrophobic and hydrophilic surfaces has been extensively investigated by soft-contact AFM imaging and force spectroscopy^{37, 46, 47}. For example, SDS at 0.5 cmc self-assembles at the HOPG-liquid interface forming linear parallel hemi-micelles. The structures observed result from the epitaxial adsorption of the initial surfactant molecules in a tail-to-tail and head-to-head fashion determined by the surface structure of HOPG⁴⁶.

It is noted that SDS is an ionic surfactant, i.e., the functional group is negatively charged and is not expected to adsorb onto the negatively charged silicon nitride AFM tip at neutral pH. SDS was purposely chosen to avoid potential complication caused by surfactant molecules adsorbed onto the tip.

The force curves show an EDL repulsion followed by a snap-in to contact at <5 nm, indicative of the size of hemi-micelles⁴⁸. Examples of such force curves between a Si_3N_4 tip and HOPG in 0.5 cmc SDS without solvent-exchange are shown in Figure 4a and a schematic of the interaction shown in Figure 4b. The slope of the data correlates well with a background electrolyte concentration of 4 mM (i.e. Debye length of 4.8 nm, which is 0.5 cmc). The force data is reproducible as hemi-micelles form evenly over the HOPG atomic layers.

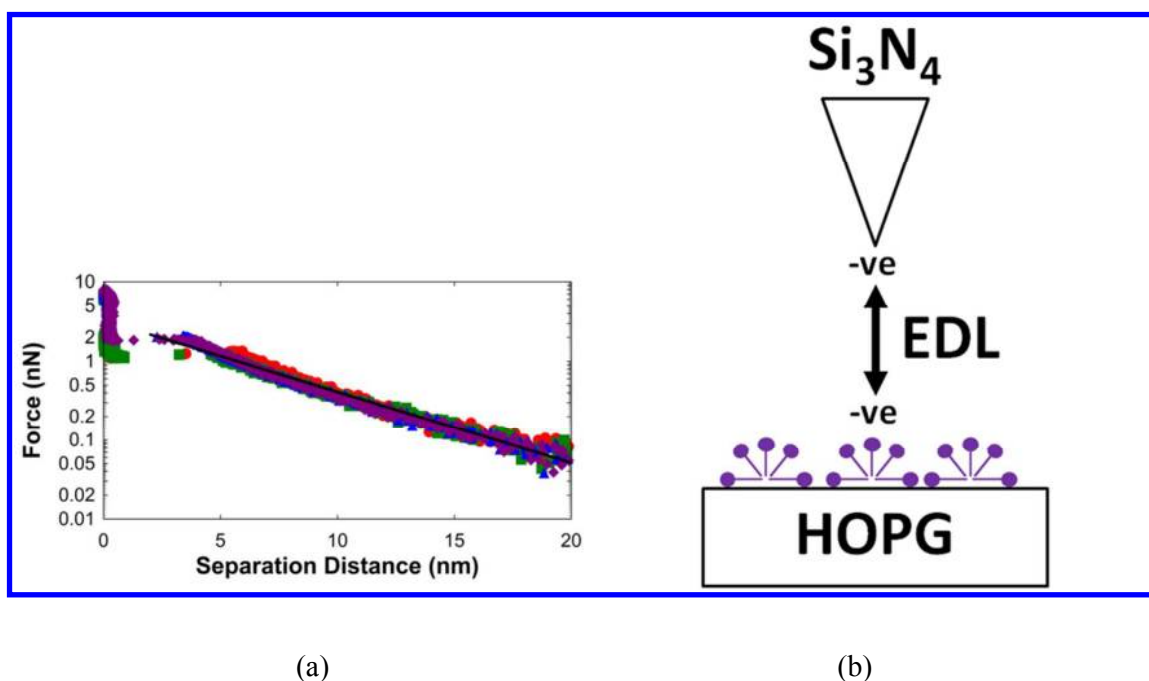
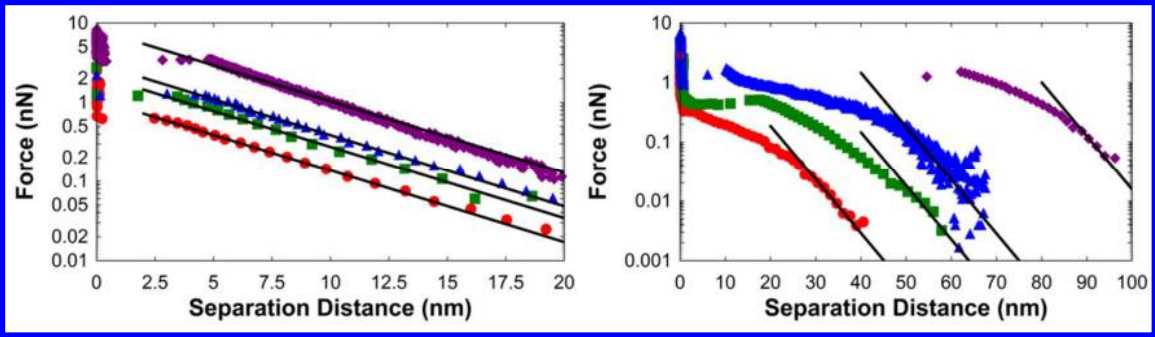


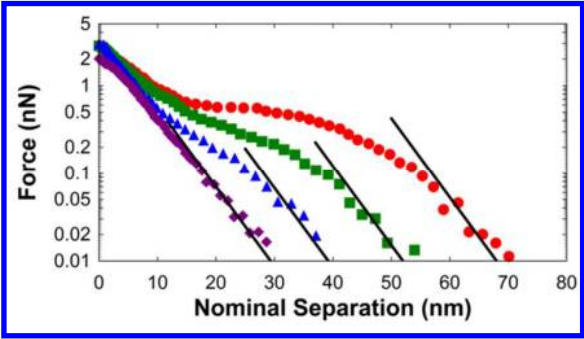
Figure 4: a) Force curves between a Si_3N_4 tip and HOPG in 0.5cmc SDS without prior solvent-exchange. Four sets of data from different experiments are shown. The black line is an exponential fit to the data with a Debye length of 4.8 nm ($\approx$ 4 mM background electrolyte). b) An illustration of the interaction, which can be characterized by an EDL repulsion and a jump-in to contact at the height of the hemi-micelles. Schemes are not to scale.

As the surfactant adsorption is governed by the surface structure of the HOPG the adsorption and self-assembly of SDS must be altered if nanobubbles and IGE are present. As expected from the significant changes in the forces in pure water after the solvent-exchange, the force is SDS dramatically alter if solvent-exchange is performed prior to addition of 0.5 cmc SDS, as shown in Figure 5. After solvent-exchange three distinct types of force curves occur, variable strength EDL repulsive force between non-deformable surfaces (Figure 5a), a variable strength EDL between deformable surfaces with a generally long range attraction (Figure 5b), and a variable strength EDL repulsion between deformable surfaces without contact (Figure 5c). As shown in the force map of jump in distance (Figure 6) the EDL force between deformable surfaces with long range attraction and without contact occur in discrete circular areas, thought to be nanobubbles covered in surfactant, while the variable strength EDL between non-deformable surfaces occurs in the remainder of the surface and is thought to be due to surfactant adsorption on the IGE.



(a)

(b)



(c)

Figure 5: Three distinct types of force curves between a silicon-nitride tip and HOPG in 0.5cmc SDS after solvent-exchange showing a) a variable strength EDL repulsion between non-deformable surfaces, b) a variable strength EDL repulsion between deformable surfaces with long range attraction and c) a variable strength EDL repulsion between deformable surfaces without contact. The black line is an exponential fit to the data with a Debye length of 4.8 nm (≈ 4 mM background electrolyte). In the case of deformable surfaces the line is fit to the data at long separation distances.

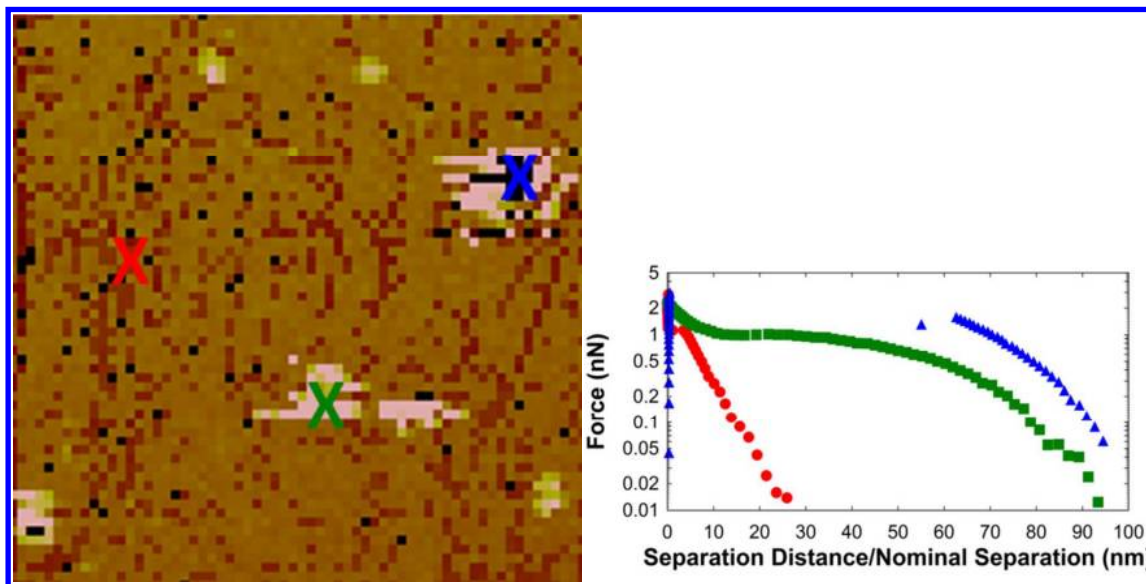


Figure 6: a) 5x5 μm AFM force map indicating strength of repulsion and jump-in to contact of HOPG in 0.5 cmc SDS after solvent-exchange and b) example force curves (the colored of the X on the force map corresponds with the color of the force data). The light areas indicate force curves with repulsion and the dark areas indicate jump-in to contact after repulsion.

In the variable strength EDL force the Debye length is the same as in the force without SDS (Figure 4), which is expected as the SDS concentration is identical. The linearity of a semi-log force vs. separation plot demonstrates that the EDL force occurs between non-deformable surfaces, thus these forces occur in a non-nanobubble area. The variable strength of the force indicates that the surface potential is not constant, suggesting that the adsorption of SDS is disturbed by the IGE resulting in differing configurations and packing of surfactant molecules, as shown schematically in Figure 7. This finding long with the variable range force in pure water implies that the IGE is not

consistent over the surface, as suggested by the bounding of micro-pancakes by HOPG cleavage steps²⁷ and the patchiness of the gas-like molecular layers²⁴.

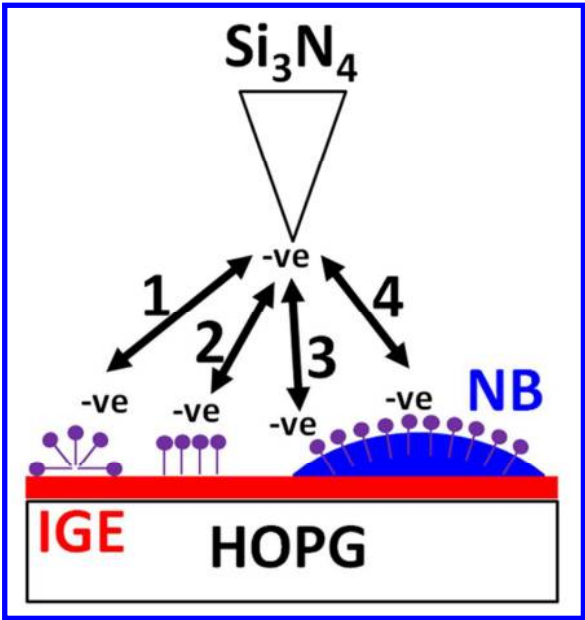
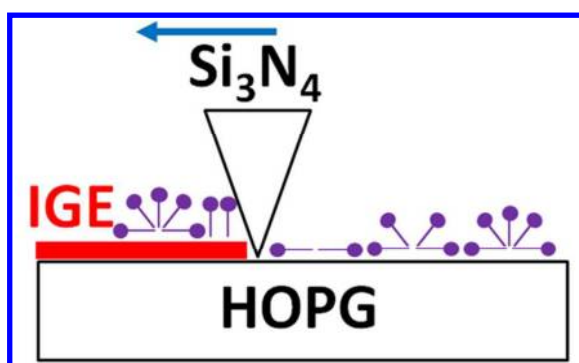


Figure 7: The interaction between a tip and a HOPG surface in 0.5cmc SDS after solvent exchange. Interaction 1 & 2 are the variable strengths EDL repulsion between non-deformable surfaces. Interaction 3 & 4 are the variable strength EDL repulsion between deformable surfaces with long range attraction. Schemes are not to scale.

For the repulsion before longer range attractive jump-in forces (Figure 5b) the deviation of the data from linearity in a semi-log force vs. separation plot suggests an EDL force with a deformable surface⁴⁹, thus these forces occur at nanobubbles. In the force map (Figure 6) the center of the larger nanobubble experiences no jump-in at all and instead experiences a repulsive resistance with no contact. No such force was found in the pure water system and suggests that the nanobubbles have become more deformable in SDS and the liquid film between the tip and nanobubble is more stable, as expected from the reduction in surface tension (50.55 mN/m⁵⁰) and surfactant stabilization of wetting films.

It is interesting that in the work of Zhang et al.²¹ the nanobubbles are displaced after SDS. For example in Figure 1²¹ of that work the location and number of domains in SDS (B1) are changed when water is flushed through the system (C1). This is probably due to the nanobubbles being less

1
2 firmly attached and the mechanical action of the oscillating tip/flowing fluid moving them, much
3 like the removal of dirt in detergency. The instability of nanobubbles is probably the reason why the
4 larger nanobubbles in the force map (Figure 6) are not as circular, as the probing of the tip probably
5 moves them. It is well known that contact mode imaging of a nanobubble covered surface can
6 coalesce and move nanobubbles in pure water⁴⁰. Can the chemical action of SDS and the
7 mechanical action of the tip completely remove nanobubbles and IGE and allow SDS to adsorb
8 directly to the HOPG surface in the hemi-micelle configuration, as described by the schematic in
9 Figure 8?
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33 Figure 8: Contact mode imaging removes nanobubbles and adsorbed gas from the HOPG surface
34 and allowed SDS molecules to arrange in a hemi-micelle configuration. Schemes are not to scale.
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37 To test this the stability of nanobubbles and IGE in SDS, a contact mode image was
38 performed over a $5 \times 5 \mu\text{m}$ area multiple times and then force curves taken within this area, as shown
39 in Figure 9. The force curves after contact mode imaging are no longer variable in strength, but the
40 same as the force curves in 0.5cmc SDS without prior solvent-exchange (Figure 4a). Such results
41 demonstrate that SDS has reabsorbed in a hemi-micelle formation as the nanobubbles and IGE have
42 been removed by the combined mechanical action of the tip and the chemical action of the SDS. It
43 appears that nanobubbles and IGE can be removed from HOPG if a strongly adsorbing molecule
44 can compete against the IGE. In a water system the reemergence of an IGE at HOPG must be faster
45 than the time required to take a force curve after contact mode imaging. In conclusion, nanobubbles
46 are stable in SDS as found by Zhang et al.²¹, but not as stable to mechanical action as in pure water.
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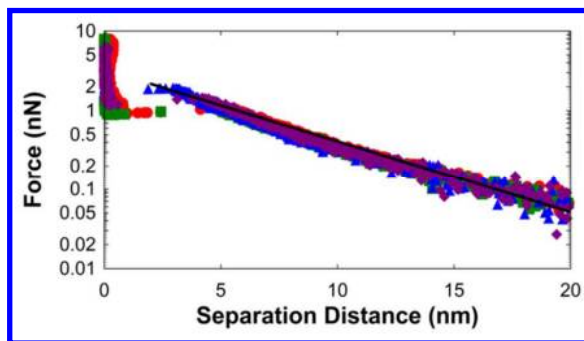


Figure 9: Force curves of between a silicon-nitride tip and HOPG in 0.5cmc SDS after solvent exchange and then within an area exposed to contact mode imaging. The black line is an exponential fit to the data with a Debye length of 4.8 nm (≈ 4 mM background electrolyte).

The results presented strongly demonstrate that nanobubbles do not sit alone at the HOPG-liquid interface. In combination with MD simulation and AFM imaging results presented by leaders in the field we agree that nanobubbles co-exist with an IGE. The strong evidence for IGE co-existing with nanobubbles validates the dynamic equilibrium model¹⁴ for meta-stability and provides a reason for the low contact angle (within the nanobubble). Currently nanobubbles have been confirmed to exist for more than 4 days². As the gas cannot be replenished without some energy source (nanobubbles are not a perpetual motion machine) longer term stability is not expected, but should definitely be tested.

4 Conclusion

Our AFM force spectroscopy study reveals that the solvent-exchange process not only creates nanobubbles in HOPG-water interfaces, but also changes the interface areas between nanobubbles from the repulsive EDL forces to non-DLVO attractive forces. These non-DLVO forces are resulted from interfacial gas enrichment (IGE) in which cannot be removed by contact mode scanning of cantilever tip in HOPG-water interfaces. However, further results show that the IGE can be removed by combining mechanical action of the tip and the chemical adsorption of the surfactant after injection of SDS solution into HOPG-water interfaces. The co-existence of nanobubbles and IGE is consistent with the transient stability of nanobubbles as proposed by Lohse and colleagues [14].

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Notes

The authors declare on competing financial interest.

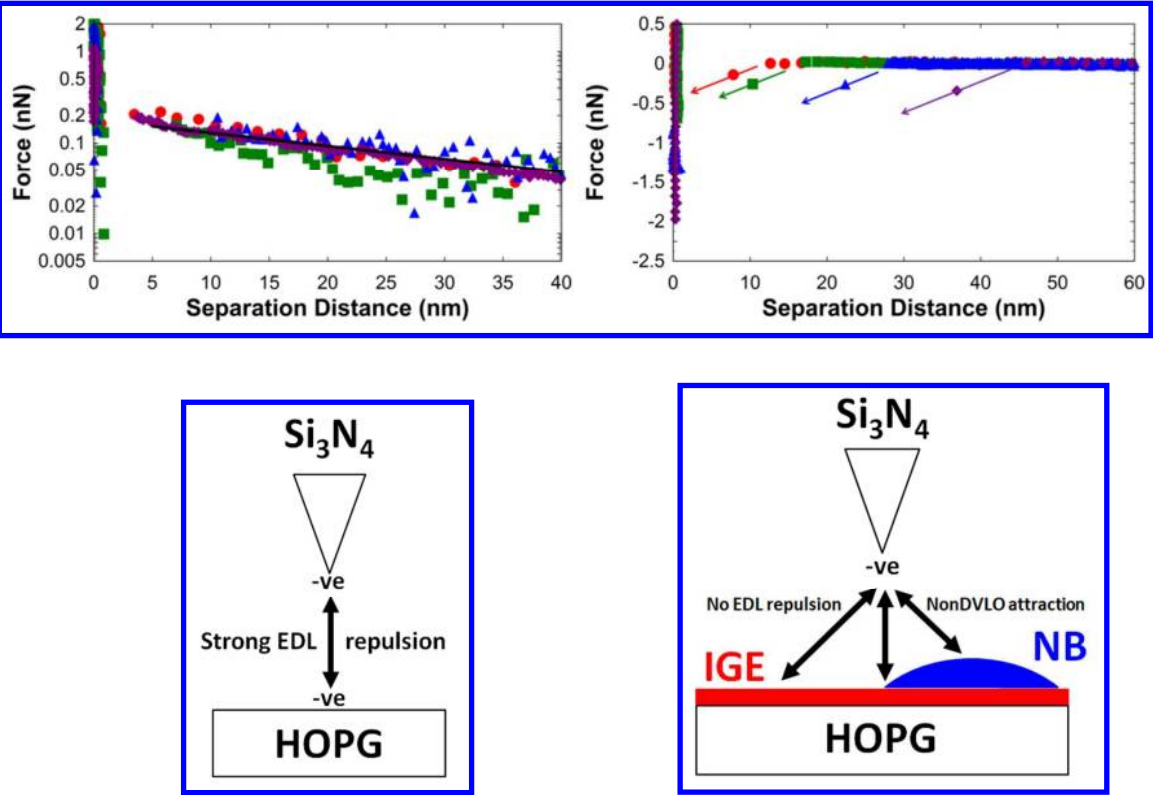
References

1. Parker, J. L.; Claesson, P. M.; Attard, P., Bubbles, cavities, and the long-ranged attraction between hydrophobic surfaces. *Journal of Physical Chemistry* **1994**, 98, (34), 8468-80.
2. Zhang, X. H.; Quinn, A.; Ducker, W. A., Nanobubbles at the Interface between Water and a Hydrophobic Solid. *Langmuir* **2008**, 24, (9), 4756-4764.
3. Zhang, X. H.; Khan, A.; Ducker, W. A., A Nanoscale Gas State. *Phys. Rev. Lett.* **2007**, 98, (13), 136101.
4. Hampton, M. A.; Nguyen, A. V., Nanobubbles and the nanobubble bridging capillary force. *Advances in Colloid and Interface Science* **2010**, 154, (1-2), 30-55.
5. Zhang, X.; Maeda, N., Interfacial gaseous states on crystalline surfaces. *Journal of Physical Chemistry C* **2011**, 115, (3), 736-743.
6. Zhang, X.; Kumar, A.; Scales, P. J., Effects of solvency and interfacial nanobubbles on surface forces and bubble attachment at solid surfaces. *Langmuir* **2011**, 27, (6), 2484-2491.
7. van Limbeek, M. A. J.; Seddon, J. R. T., Surface nanobubbles as a function of gas type. *Langmuir* **2011**, 27, (14), 8694-8699.
8. Song, B.; Walczyk, W.; Schoenherr, H., Contact angles of surface nanobubbles on mixed self-assembled monolayers with systematically varied macroscopic wettability by Atomic Force Microscopy. *Langmuir* **2011**, 27, (13), 8223-8232.

9. Seddon, J. R. T.; Lohse, D., Nanobubbles and micropancakes: gaseous domains on immersed substrates. *Journal of Physics-Condensed Matter* **2011**, 23, (13).
10. Hampton, M. A.; Nguyen, A. V., The Nanobubble Story. In *Encyclopedia of Surface and Colloid Science, Second Edition*, Taylor & Francis: 2012; pp 1-15.
11. Seddon, J. R. T.; Kooij, E. S.; Poelsema, B.; Zandvliet, H. J. W.; Lohse, D., Surface bubble nucleation stability. *Physical Review Letters* **2011**, 106, (5).
12. Seddon, J. R. T.; Zandvliet, H. J. W.; Lohse, D., Knudsen gas provides nanobubble stability. *Physical Review Letters* **2011**, 107, (11), 116101.
13. Ducker, W. A., Contact angle and stability of interfacial nanobubbles. *Langmuir* **2009**, 25, (16), 8907-8910.
14. Brenner, M. P.; Lohse, D., Dynamic equilibrium mechanism for surface nanobubble stabilization. *Physical Review Letters* **2008**, 101, (214505), 214505.
15. Das, S., Effect of impurities in the description of surface nanobubbles: Role of nonidealities in the surface layer. *Physical Review E* **2011**, 83, (6).
16. Das, S.; Snoeijer, J. H.; Lohse, D., Effect of impurities in description of surface nanobubbles. *Physical Review E* **2010**, 82, (5), 8.
17. Weijs, J. H.; Snoeijer, J. H.; Lohse, D., Formation of surface nanobubbles and the universality of their contact angles: a molecular dynamics approach. *Phys. Rev. Lett.* **2012**, 108, (10), 104501.
18. Zhang, X.; Chan, D. Y. C.; Wang, D.; Maeda, N., Stability of interfacial nanobubbles. *Langmuir* **2013**, 29, (4), 1017-1023.
19. Weijs, J. H.; Lohse, D., Why surface nanobubbles live for hours. *Phys. Rev. Lett.* **2013**, 110, (5), 054501.
20. Liu, Y.; Zhang, X., Nanobubble stability induced by contact line pinning. *J. Chem. Phys.* **2013**, 138, (1), 014706.
21. Zhang, X.; Uddin, M. H.; Yang, H.; Toikka, G.; Ducker, W.; Maeda, N., Effects of surfactants on the formation and the stability of interfacial nanobubbles. *Langmuir* **2012**, 28, (28), 10471-10477.
22. Dammer, S. M.; Lohse, D., Gas enrichment at liquid-wall interfaces. *Phys. Rev. Lett.* **2006**, 96, (20), 206101.
23. Chun-Lei, W.; Zhao-Xia, L.; Jing-Yuan, L.; Peng, X.; Jun, H.; Hai-Ping, F., High density gas state at water/graphite interface studied by molecular dynamics simulation. *Chinese Physics B* **2008**, 17, 2646.
24. Lu, Y.-H.; Yang, C.-W.; Hwang, I.-S., Molecular layer of gaslike domains at a hydrophobic-water interface observed by frequency-modulation atomic force microscopy. *Langmuir* **2012**, 28, (35), 12691-12695.
25. Seddon, J. R. T.; Bliznyuk, O.; Kooij, E. S.; Poelsema, B.; Zandvliet, H. J. W.; Lohse, D., Dynamic dewetting through micropancake growth. *Langmuir* **2010**, 26, (12), 9640-9644.
26. Zhang, L.; Zhang, X.; Fan, C.; Zhang, Y.; Hu, J., Nanoscale multiple gaseous layers on a hydrophobic surface. *Langmuir* **2009**, 25, (16), 8860-8864.
27. Hampton, M. A.; Nguyen, A. V., Accumulation of dissolved gases at hydrophobic surfaces in water and sodium chloride solutions: Implications for coal flotation. *Minerals Engineering* **2009**, 22, (9-10), 786-792.
28. Zhang, X. H.; Maeda, N.; Hu, J., Thermodynamic stability of interfacial gaseous states. *Journal of Physical Chemistry B* **2008**, 112, (44), 13671-13675.
29. Zhang, X. H.; Zhang, X.; Sun, J.; Zhang, Z.; Li, G.; Fang, H.; Xiao, X.; Zeng, X.; Hu, J., Detection of novel gaseous states at the highly oriented pyrolytic graphite-water interface. *Langmuir* **2007**, 23, (4), 1778-1783.
30. Zhang, X. H.; Maeda, N.; Craig, V. S. J., Physical properties of nanobubbles on hydrophobic surfaces in water and aqueous solutions. *Langmuir* **2006**, 22, (11), 5025-5035.
31. Seddon, J. R. T.; Lohse, D.; Ducker, W. A.; Craig, V. S. J., A deliberation on nanobubbles at surfaces and in bulk. *ChemPhysChem* **2012**.

32. Borkent, B. M.; de Beer, S.; Mugele, F.; Lohse, D., On the shape of surface nanobubbles. *Langmuir* **2009**, 26, (1), 260-268.
33. Lou, S.; Gao, J.; Xiao, X.; Li, X.; Li, G.; Zhang, Y.; Li, M.; Sun, J.; Li, X.; Hu, J., Studies of nanobubbles produced at liquid/solid interfaces. *Materials Characterization* **2002**, 48, (2/3), 211-214.
34. Lou, S.-T.; Ouyang, Z.-Q.; Zhang, Y.; Li, X.-J.; Hu, J.; Li, M.-Q.; Yang, F.-J., Nanobubbles on solid surface imaged by atomic force microscopy. *Journal of Vacuum Science & Technology, B: Microelectronics and Nanometer Structures* **2000**, 18, (5), 2573-2575.
35. Zhang, X. H.; Zhang, X. D.; Lou, S. T.; Zhang, Z. X.; Sun, J. L.; Hu, J., Degassing and temperature effects on the formation of nanobubbles at the mica/water interface. *Langmuir* **2004**, 20, (9), 3813-3815.
36. Cleveland, J. P.; Manne, S.; Bocek, D.; Hansma, P. K., A nondestructive method for determining the spring constant of cantilevers for scanning force microscopy *Review of Scientific Instruments* **1993**, 64, (2), 403-405.
37. Paruchuri, V. K.; Nguyen, A. V.; Miller, J. D., Zeta-potentials of self-assembled surface micelles of ionic surfactants adsorbed at hydrophobic graphite surfaces. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2004**, 250, (1-3 SPEC. ISS.), 519-526.
38. Arai, T.; Aoki, D.; Okabe, Y.; Fujihira, M., Analysis of surface forces on oxides in aqueous solutions using AFM. *Thin Solid Films* **1996**, 273, (1-2), 322-326.
39. Pocsik, I.; Veres, M.; Fule, M.; Toth, S.; Koos, M., Charge-Generated Changes in Graphite Structures. *arXiv preprint cond-mat/0307476* **2003**.
40. Hampton, M. A.; Donose, B. C.; Nguyen, A. V., Effect of alcohol–water exchange and surface scanning on nanobubbles and the attraction between hydrophobic surfaces. *J Colloid Interface Sci.* **2008**, 325, (1), 267-274.
41. Ishida, N.; Inoue, T.; Miyahara, M.; Higashitani, K., Nano bubbles on a hydrophobic surface in water observed by tapping-mode atomic force microscopy. *Langmuir* **2000**, 16, (16), 6377-6380.
42. Taran, E.; Hampton, M. A.; Nguyen, A. V.; Attard, P., Anomalous time effect on particle-bubble interactions studied by atomic force microscopy. *Langmuir* **2009**, 25, (5), 2797-2803.
43. Preuss, M.; Butt, H. J., Direct measurement of particle-bubble interactions in aqueous electrolyte: Dependence on surfactant. *Langmuir* **1998**, 14, (12), 3164-3174.
44. Nguyen, A. V.; Evans, G. M., Attachment interaction between air bubbles and particles in froth flotation. *Experimental Thermal and Fluid Science* **2004**, 28, (5), 381-385.
45. Graciaa, A.; Morel, G.; Saulner, P.; Lachaise, J.; Schechter, R. S., The ζ -potential of gas bubbles. *Journal of Colloid and Interface Science* **1995**, 172, (1), 131-136.
46. Wanless, E. J.; Ducker, W. A., Organization of sodium dodecyl sulfate at the graphite-solution interface. *J. Phys. Chem.* **1996**, 100, (8), 3207-3214.
47. Paruchuri, V. K.; Nalaskowski, J.; Shah, D. O.; Miller, J. D., The effect of cosurfactants on sodium dodecyl sulfate micellar structures at a graphite surface. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2006**, 272, (3), 157-163.
48. Paruchuri, V. K. Surface micelles as revealed by soft contact atomic force microscopy imaging. The University of Utah, 2009.
49. Attard, P.; Miklavcic, S. J., Effective spring description of a bubble or a droplet interacting with a particle. *Journal of Colloid and Interface Science* **2002**, 247, (1), 255-257.
50. Ozdemir, O.; Karakashev, S. I.; Nguyen, A. V.; Miller, J. D., Adsorption and surface tension analysis of concentrated alkali halide brine solutions. *Minerals Engineering* **2009**, 22, (3), 263-271.

GRAPHIC ABSTRACT



Forces between an AFM tip and a bare HOPG in water (left) or a HOPG after water-ethanol exchange (right)