The Morphology and Stability of Nanoscopic Gas States at Water/Solid Interfaces

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Nanoscale gas bubbles have surprising stability at water/solid surfaces. Herein, we summarize progress made on investigating gases at the water/solid interfaces on the nanometer scale. The gas states include nanobubbles, micropancakes, multiple gas layers and their coexistence; these were investigated from experimental and theoretical aspects. The stability of nanoscale gas bubbles may be attributed to high inner density, as observed in molecular dynamic simulations and theoretical analysis. Moreover, it was found that there were maximal length scales for stable nanobubbles, namely, 100 nm high and a curvature radius of 2 μm.

1. Introduction

Research on interfacial nanoscale gas states, including bubbles and micropancakes, in aqueous solutions has become a very hot topic due to their significance in surface science, biological science, nanotechnology, medical science, and industry.[1] These surface nanoscale bubbles are spherical cap shapes, with typical heights and curvature radii of 5–100 nm and 100–2000 nm, respectively, whereas micropancakes are several microns in diameter but restricted to only 1–10 nm high.[2] Furthermore, multilayer micropancakes and nanobubble-micropancake composites have also been discovered.[2c, d] Nanobubbles are quite stable at liquid/solid surfaces, even under substantially reduced liquid pressures.[3] Their lifetimes can reach several days without any change in morphology; these are known as "superstable nanobubbles". Compared with nanobubbles, micropancakes seem to be less stable and may quickly turn into bubbles over time.[2a]

However, the stable existence of nanobubbles at the water/solid interface is hard to understand with classical thermodynamics.[4] The traditional Laplace–Young equation predicts that the pressure inside a nanobubble is extremely high (e.g. 144 atm for a bubble with a radius of 10 nm in water).[4a] The lifetime predicted by conventional thermodynamics only ranges from several picoseconds to hundreds of microseconds, which is too short to be observed experimentally.[5]

Problems and debates also exist for nanobubble experiments. The major question is as follows: are the nanobubbles we observe really gas bubbles? Although many experiments with indirect measurements, such as optical and neutron or X-ray scattering, suggested the existence of gas nanobubbles,[6] negative conclusions were also reported with the same systems and same methods.[7] This disagreement might come from the poor repeatability in nanobubble production in those systems together with difficulties in the analysis of indirect measurements. Atomic force microscopy (AFM) in tapping mode gave more direct evidence by imaging nanobubbles on various surfaces.[8] However, some argued that AFM could not distinguish between gas nanobubbles and possible soft contaminants deposited on the surface during sample preparation because AFM has an intrinsic limitation in that it mostly gives information on the morphological and mechanical properties of the sample.[7]

Since there is still a lack of direct measurements for detecting the chemical composition inside the nanobubbles based on current methods, we believe that repeatable production of a sufficient amount of nanobubbles on surfaces together with control degassing experiments are necessary to avoid ambiguity in the nanobubble experiments. Degassing helps us to distinguish between gas nanobubbles and contamination. In addition, a large amount of nanobubbles enables more distinctive and conclusive comparative statistical analyses with and without degassing. Recently, well-controlled experiments revealed two key pieces of evidence, which indicated that the soft domains observed by AFM did have dissolved gas inside. For example, nanobubbles did not form with degassed water and degassing in situ led to their removal.[9] More important evidence came from electrolysis experiments.[10] The formation of nanobubbles could be controlled by reaction time and voltage; hydrogen or oxygen gas were only produced at the electrode surface in electrochemical reactions. These experiments have been repeated in different laboratories and the results

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lead us to believe that nanobubbles do contain dissolved gas and can exist stably at water/solid surfaces.\[18\]

Why are nanobubbles stable? There are several hypotheses. Bunkin et al. suggested that charges on the surface of a sub-microbubble could provide stabilization.\[11\] However, Zhang et al. did not find any significant effects on the stability of nanobubbles when the salts and acids in the solution were changed.\[24\] Simonsen et al. argued that the lifetime of nanobubbles would become longer if they had large radii when the contact angles were very small.\[12\] Recently, Brenner and Lohse proposed a theory for nanobubble stability that involved flux of gas from solution to a hydrophobic surface.\[13\] This gas passes into the nanobubble and compensates for loss of gas from the bubble. The balance is only stable for a given amount of supersaturation of the bulk liquid such that small fluctuations die away and the system can be described as being in a dynamic equilibrium. Therefore, although there are numerous explanations for the long lifetime of nanobubbles observed experimentally, the problem is still not satisfactorily resolved.\[14\]

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layers) and try to understand why surface nanobubbles can be very stable and the length of this stability. Results suggested that higher gas density inside the nanobubbles might be one of the reasons for their long lifetimes. Nanobubbles might be unstable if their heights are up to 100 nm or curvature radii exceed 2 μm.

2. Various Gas States at the Nanometer Scale

In 2000, surface nanobubbles with spherical cap shapes were first detected by tapping mode AFM.\(^\text{16}\) These nanobubbles were several or tens of nanometers high and hundreds of nanometers long and could survive for at least 5 days under constant ambient conditions.\(^\text{14}\) Later, Zhang et al. found that domains with very flat tops, called micropancakes, could be formed on atomically flat graphite surfaces by exchanging ethanol and water or cold water and hot water.\(^\text{2d}\) They were less than 1 nm high, but several microns long. More recently, we observed that gas could exist at the water/highly oriented pyrolytic graphite (HOPG) interface in the form of multiple gaseous layers, such as bi- and trilayers.\(^\text{24}\) As shown in Figure 1, the bilayers are composed of two flat layers, whereas the trilayers have another less flat layer sitting on top of the two flat layers. We found that the apparent heights of each layer in the bi- and trilayers changed with experimental conditions. Generally, the layer near the surface was thinner than those far from the surface.

To explore the relationship between gas micropancakes, nanobubbles, and multiple gas layers, we analyzed the states of gas accumulated at the water/solid interface,\(^\text{17}\) as inspired by the theory of liquid wetting on solid surfaces reported by de Gennes et al.\(^\text{18}\) In continuum theory, the Hamaker constant was used to describe long-range interactions at the microscopic scale. We found three possible gas states at the water/solid interface, corresponding to those observed by AFM experiments: gas pancake (Figure 2a), gas bubble, and gas bubble(s) coexisting with a gas pancake (Figure 2b). Interestingly, we found that nanobubbles on micropancakes could be moved by the tip; therefore, it was possible that a very thin layer of water stabilized nanobubbles and micropancakes. The relationship between nanobubbles and micropancakes needs to be explored further.

We investigated the stability of nanobubbles and gas layers with time. Figure 3 shows a series of in situ tapping mode AFM images acquired by continuously scanning at a very low load (near the pull-off force). The results showed that a pancake-like gas layer changed into nanobubbles on a HOPG substrate in water with the help of an AFM tip. The gas areas covering the HOPG substrate gradually decreased, followed by an increase in the heights of the pancake-like gas layers and finally nanobubbles formed after a longer scanning time (Figure 3e). We can therefore conclude that gas layers are unstable compared with nanobubbles under the same conditions and can slowly change into nanobubbles after a certain time. Scanning with an AFM tip speeds up this translation process.

Figure 1. Tapping mode AFM images of gas trilayers at the water–HOPG interface. The height image (a) and the section analysis (b) of trilayers obtained after injecting \((4 \times 2)°\) water on HOPG with a temperature of \((40 \pm 2)°\) C. Scan size: \(3.1 \mu m \times 3.1 \mu m\), data scale: 20 nm. The height image (c) and the section analysis (d) of trilayers obtained by exchanging ethanol and salt solution at room temperature. 1 and 2 indicate the first and the second layer, respectively. The image was taken in NaCl solution (0.1 m). Scan size: \(12 \mu m \times 12 \mu m\), data scale: 80 nm.

3. High Inner Density of Nanobubbles: A Possible Reason for Nanobubble Stability

Water exhibits special properties when it is in a confined space. For example, Hu et al. found that the first layer of water molecules formed hexagonal or ice-like structures on atomically flat mica surfaces at room temperature.\(^\text{19}\) Water changes from a first-order phase transition—a liquid to bilayer amorphous transition—above the freezing temperature of bulk
The densities of both gas states are very used and the simple point charge (SPC) water model was interface by using molecular dynamics simulations with a also reported that gas could be enriched near the hydrophobic the nanometer scale may be a new phase. Dammer and Lohse temperature increases.

What about gas on the nanometer scale at water/solid inter-
faces? We studied the accumulation behavior of N₂ and H₂ at water/graphite interfaces by molecular dynamics simulations under ambient temperature and pressure.[21] The initial gas concentrations was set as supersaturated. The accumulation states of two kinds of gases, N₂, the main content of air, and H₂ were studied. Gromacs 3.2.1 and a universal force field were used and the simple point charge (SPC) water model was chosen.[22] Surprisingly, the densities of both gas states are very high, even comparable with that of liquid N₂ and H₂. For example, the N₂ nanobubbles at the water/graphite interface showed that the inner density of the nanoscale N₂ bubble was about 41% of liquid N₂ (Figure 4). The model in Figure 4a (water molecules are omitted) is that of frozen graphite with a size of 9,715×9,869 nm² (3852 carbon atoms per sheet) parallel to the x-y plane. Initially, 800 N₂ molecules, which form a simple cubic structure with a lattice constant of 1.227 nm, with a minimal distance of 3.0 Å above graphite are immersed in box full of water molecules. The system is in an isothermal–isobaric ensemble (NPT, 1 atm and 300 K). N₂ molecules form a spherical shape above the graphite surface (Figure 4a) when the system reaches equilibrium, while the average radius of the bottom of the bubble is independent of time, as shown in Figure 4b. The density profile along the z axis is shown in Figure 4c, with two distinct density peaks at distances of around 0.35 and 0.70 nm. The average density is approximately 340 kg m⁻³ in the region of 1.0 nm < z < 2.5 nm. We also verified whether the densities of gas bubbles were sensitive to environment temperatures (Figure 4d). Clearly, temperature affects the densities of gas bubbles; the density decreases as the temperature increases.

These results suggest that the materials in the bubbles on the nanometer scale may be a new phase. Dammer and Lohse also reported that gas could be enriched near the hydrophobic interface by using molecular dynamics simulations with a simple L–J liquid and hydrophobic wall.[23] They reported that gas enrichment in the vicinity of the hydrophobic surface was more than two orders of magnitude when compared with the density in the bulk liquid. They also indicated that gas enrichment resembled surface nanobubbles. The heights of those nanobubbles were in the order of the molecule diameter, σ, which was much lower than that reported by AFM experiments. In our system, the typical height of the nanobubbles was about 2.0 nm, which approached the heights that could be observed by AFM. Sedmeier et al. reviewed simulations of the properties of interfacial water at hard hydrophobic and -philic surfaces.[24] Our results are consistent with the model reported in this review that the nonpolar surface was hydrophobic for polar water molecules. However, it should be noted that three phases—water, N₂, and graphite—coexisted in our system and thus interactions were complicated and different from that of two phases—surface and water—mentioned in this review.

Then we analyzed gas aggregation on a solid surface using continuum theory and found that densities of the gases inside the nanobubbles may vary with respect to the distance to the solid surface. Interestingly, using a mathematical method, we demonstrated that the existence of a gas pancake did not significantly depend on the change of the density.[17]

If gas bubbles on the nanometer scale had a high inner density, what about their lifetime? Based on diffusion theory for macroscopic bubbles,[5] we analyzed the lifetime of nanoscale bubbles with a large inner density by supposing Henry’s law was suitable on this scale and an empirical relationship between surface tension and the densities of liquid and vapor suggested by MacLeod and Sugden was adopted.[25] The relationship for surface tension is \( \gamma = \frac{A M_1 \cdot \gamma_{o}}{M_2} \), in which \( M, A, \) and \( \rho_1 \) are molecular weight (in kg mol⁻¹), parachor, and the density of liquid (in kg m⁻³), respectively.[26] The gas bubble system studied is shown in Figure 5.

Finally, the lifetime of the bubble is obtained from \( t_i = \frac{4k}{D} \left( \frac{1}{\gamma_{o} \rho_1} \right) \), in which \( R_i \) is initial radius of bubble, \( D \) is the coefficient of diffusivity of the gas inside the liquid, \( k \) is Henry’s constant (in Pa m³ kg⁻¹), and \( \gamma_{o} \) is the surface tension of the liquid at the macroscopic scale.

Taking N₂ nanobubbles in water as an example, Figure 6 shows the lifetime with respect to the inner density of a N₂ bubble with several typical radii. In the following calculations, \( k = 5.57 \times 10^{6} \text{ Pa m}^{3} \text{ kg}^{-1} \cdot \text{s}^{-1} \), \( D = 2 \times 10^{-9} \text{ m}^{2} \text{ s}^{-1} \), \( \gamma_{o} = 72 \text{ mN m}^{-1} \), and \( \rho_1 = 1 \times 10^{3} \text{ kg m}^{-3} \) at room temperature and 1 atm.[20] The results showed that the stability of the bubble was greatly enhanced when the inner density increased. When \( R_i \) was only 30 nm, the lifetime increased from 0.2 μs to 1.1 ms if the density changed from 0.15 to 60% of the density of liquid nitrogen. If we follow the suggestion proposed by Simonsen et al.,[12] in which the curvature radii of the nanoscale bubbles is large and even reach the micrometer scale, the lifetime will increase from 0.2 ms to 1.4 s when the density changes from 0.15 to 60% of the density of the liquid nitrogen for a nanobubble radius of 322 nm. This lifetime approaches the timescale of the experimental observations.
It should be noted that the exact value for the lifetime may differ because we need to consider more effects and re-evaluate the rules for the nanoscale, including the empirical relationship between surface tension and densities of liquid and vapor, and Henry’s law in the case of a large density of gas.

However, the conclusion of the great enhancement of the lifetime due to the high inner density remains valid.

It must be pointed that the mechanism for the stability of the nanobubbles may have multiple causes and different factors work under different conditions or they work together to contribute to the stability.

To demonstrate the importance of the interface to the stability of the nanobubbles, we have examined all data published in the literature and performed new experiments. We calculated contact angles, curvature radii, and base radii of nanobubbles, as defined in Figure 7, by measuring the heights of nanobubbles. These nanobubbles were produced by ethanol–water exchange and electrochemistry on atomically flat graphite or mica surfaces. The contents of the nanobubbles were air or hydrogen.

The range of the contact angles was from 5 to 60° on both hydrophilic mica and hydrophobic HOPG surfaces (Figure 8). This corresponds to contact angles of liquid on solid ranging from 120 to 175°, obtained by subtracting 180° from the contact angles of the gas nanobubbles. The contact angles of the nanoscale bubbles were much smaller than those of macroscopic bubbles; this is consistent with previous results. [8b, 10b, 27] It was also found that the contact angles of gas nanobubbles increased nearly linearly with their heights; this suggests that the contact angle of a nanobubble has a tendency toward a macroscopic value as the height of the bubble increases. More interestingly, the radii of curvature were less than 300 nm for most air nanobubbles on hydrophilic mica surfaces, but they were between 100 and 1600 nm for air or hydrogen nanobubbles on hydrophobic HOPG surfaces. The heights of the nanobubbles were less than 100 nm. These results indicated that stable nanobubbles may have had an upper limit on the length scale.

The existence of a maximum length for stable nanobubbles is further supported by results for nanobubbles controllably produced by an electrochemical method. The advantage of this method is that the sizes of the nanobubbles can be tuned by varying either the applied voltage or the reaction time. Generally, lower voltages resulted in larger average sizes for
the nanobubbles after a sufficiently long reaction time. The heights and curvature radii of these nanobubbles were less than 100 nm and 2.0 μm, respectively. More interestingly, AFM experiments observed many blank circular areas in which almost no nanobubbles existed after loading voltages of about $V_C = 1.8$ V for around 5 s. These blank circular areas were surrounded by smaller, dense nanobubbles (Figure 9a). It was pre-
sumed that these blank areas were caused by the departure of gas bubbles from the surface. The smallest radius observed for the blank areas was about 600 nm, which was close to the maximum base radius for hydrogen nanobubbles (≈450 nm) produced by using the electrochemical method, as shown in Figure 9b. The radius of curvature of the gas bubble corresponding to this smallest circular blank area was about 2 μm, if the fitting was extrapolated to a base radius of 600 nm for hydrogen nanobubbles on HOPG surfaces (Figure 9b). The results shown in Figures 8 and 9 suggest that a nanoscale gas bubble always has curvature radii of less than 2 μm and a height of less than 100 nm, suggesting possible instability for nanobubbles beyond these length scales.

Here, we emphasize that our results were obtained at room temperature and 1 atm on atomically flat surfaces of mica and HOPG without chemical modification. Nanobubble heights above 100 nm have been reported on rougher solid surfaces, which induces complicated behavior.[9] Recently, Zhang and Ducker found that the maximum heights of nanobubbles produced by the exchange of ethanol and water were about 250 nm on talc crystalline surfaces, but were about 50 and 100 nm on MoS₂ and HOPG surfaces, respectively.[28]

5. Summary and Outlook

We presented our recent progress on studying gas states at the nanometer scale, including nanobubbles, micropancakes, multiple gas layers, and their coexistence. We showed the existence of possible high-density nanoscale gas bubbles at water/solid surfaces by molecular dynamics simulations. Based on theoretical analyses, the lifetime of the nanobubbles would greatly increase and even approach the timescale for experimental observations if the inner density of the nanobubbles was high enough. AFM results indicated that the sizes of the nanobubbles had an upper limit of around 100 nm high and a curvature radius of about 2 μm. We also noted that the average inner density of CO₂ nanobubbles was (44 ± 16) mol m⁻³, which was close to that of the gas at the macroscopic scale, and the pressure was about (1.1 ± 0.4) atm, as reported by Zhang et al.[29] Because CO₂ is easily dissolved in water (the solubility of CO₂ is 0.8 L L⁻¹) and the lifetime of CO₂ gas nanobubbles was less than 2 h, as reported in reference [16], we think that the mechanism for the stability of CO₂ nanobubbles may be different from that of other less soluble gases with very long lifetimes.

Investigations into gas states at the nanometer scale have still a long way to go. We think that the high inner density of the nanobubbles is one of the most important properties to be explored. If it were true, it would have significant impact on both basic science and industrial applications. The high inner density may result from molecular interactions (van der Waals and electrostatic interactions) at the nanoscale. This is consistent with the existence of the maximum height of the nanobubbles we observed experimentally, although we note that the maximum heights of the nanobubbles were comparable to but still much larger than the length of van der Waals and electrostatic interactions (30–300 Å) reported by de Gennes.[30] Further studies are required in this direction. Therefore, the key question is how to determine chemical information and gas densities of nanobubbles experimentally. With the development of new techniques in synchrotron radiation, we believe that it is possible to image nanoscale gas bubbles and detect the content of bubbles inside. Neutron scattering is also another useful tool to measure the density of gas states near the water/solid interface. All of these answers will help to explain the stability of nanometer gas states and allow the development of new theories for gas aggregation on the nanometer scale at interfaces.

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