Cavitation nuclei at water-gold interfaces

M. Holmberg
Danish Fundamental Metrology (DFM), Matematiktorvet
307, DK-2800 Kgs. Lyngby, Denmark
mh@dfm.dtu.dk

A. Kühle
Danish Fundamental Metrology (DFM), Matematiktorvet
307, DK-2800 Kgs. Lyngby, Denmark
ak@dfm.dtu.dk

J. Garnæs
Danish Fundamental Metrology (DFM), Matematiktorvet
307, DK-2800 Kgs. Lyngby, Denmark
jg@dfm.dtu.dk

A. Boisen
MIC (Mikroelektronik Centret), Technical University of
Denmark, Ørsteds Plads 345 E, DK-2800 Kgs. Lyngby,
Denmark
ab@mic.dtu.dk

K.A. Mørch
Department of Physics and the
Quantum Protein Center, Building
309, Technical University of
Denmark, DK-2800 Kgs. Lyngby,
Denmark
morch@fysik.dtu.dk

ABSTRACT
Atomic force microscopy (AFM) investigations of gold surfaces made by evaporation of gold onto substrates of mica reveal that, when submerged in water, numerous flat, gaseous voids of nanoscale dimensions are developed at the water-gold interface. Their size, shape and distribution are recorded. Further, surface pits and grooves are found to contain gas pockets. At exposure to tensile stress such voids act as cavitation nuclei. The response of an AFM tip, submerged in liquid, to contact with the surface of an interfacial void is explained from an analysis of the balance of forces at the tip apex. The cone angle of the tip, its hydrophilicity and the force applied during scanning in contact mode are the factors decisive for achieving a topographic recording of the surface of a void. The force balance model presented explains not only the present results, but also earlier ones in which the presence of voids was revealed by force spectroscopy, while imaging was not possible [1].

INTRODUCTION
The nature of cavitation nuclei has been a question of debate since Harvey et al. [2] presented their model of stabilisation of gas nuclei in cracks and crevices of solid surfaces. Another model, the skin model, assumes that an organic skin on the surface of free gas bubbles is able to stabilise these [3], but such substances have never been identified. A model predicting gas bubble stabilisation by assuming the surface tension $\gamma$ of the liquid to be radius dependent [4] seems physically unrealistic (Cav2003-GS-4-005). However, the Harvey model has proved able to interpret a number of experimental results, e.g. effects of pressurisation [2-5] and filtration [6]. A revised Harvey-type model relates interfacial voids to concave surface elements of solid particles and structures submerged in liquids, and it shows that they may grow by broad band resonance vibrations [7-8]. Actually, investigations by scanning tunnelling microscopy (STM) of surfaces of tungsten, titanium nitride, and vapour-deposited gold on copper have revealed that when submerged in water they appear smoother than in air, which indicates the occurrence of interfacial voids at concave surface elements [9-10]. AFM force spectroscopy has proved able to identify interfacial voids on roughly polished stainless steel specimens submerged in water, but imaging of the voids was not achieved as the tip snapped onto the solid surface at contact with the voids [1].

A number of other theoretical [11-12-13] and experimental works [14-15-16-17-18-19] arguing the existence of nanobubbles have been published, but in experiments with force spectroscopy, specimen surfaces and probes were modified to be highly hydrophobic. Imaging was made in tapping mode with standard AFM probes (tip apex radius 10-20 nm), while force spectroscopy was performed with highly hydrophobic spheres of a radius of about 5-10 $\mu$m attached to the tip apex [18-19].

In this paper we present results from AFM contact mode imaging and local force spectroscopy performed on gold surfaces immersed in pure water (Milli-Q water) after being stored in air. The combination of contact mode imaging and local force spectroscopy using standard silicon probes provides possibilities of investigating the interaction between the probe tip and the nanobubbles in detail.

AFM TECHNIQUE FOR THE IMAGING OF INTERFACIAL VOIDS
Contact mode AFM is used for the imaging of the surface topography of solid structures on a nanoscale. The cantilever carrying the pointed tip, which is in contact with the surface is made to maintain a fixed deflection during horizontal scanning of the topography. This is done by servo-controlled vertical adjustments of the distance between specimen and cantilever base in order to compensate for the variations of height of the
surface. If the surface of an interfacial void, attached to a submerged specimen surface, is able to produce the cantilever deflexion required, the surface of the void is imaged instead of that of the solid. Thus, it is the force balance at the locus of tip-void contact that determines if it is possible to depict a gaseous interfacial void.

Figure 1 shows an AFM tip with an apex radius \( r_t \) which terminates a cone of half angle \( \alpha_t \). It is in equilibrium contact with an interfacial void that has the radius of curvature \( r_v \). The void shape is modified in the neighbourhood of the locus of tip-void contact to satisfy the wetted contact angle \( \theta \) of the liquid. Here the tangent to the tip surface has the angle \( \alpha \) with the tip axis. The force balance for the tip-void contact on the apex is governed by the vertical component of the surface tension force

\[
(F_{\text{AFM}}) = 2\pi r_t \cos \alpha \cdot \gamma \cdot \cos(\alpha + \theta)
\]

and the excess pressure \( \Delta p = 2\gamma / r_v \) in the void giving a vertical force

\[
F_p = \pi (r_t \cos \alpha)^2 2\gamma / r_v.
\]

These forces have to balance the force \( F_{\text{AFM}} \) imposed by deflection of the AFM cantilever carrying the tip. Thus,

\[
r_t \cos \alpha / r_v + \cos(\alpha + \theta) = F_{\text{AFM}} / (2\pi r_t \cos \alpha) \tag{1}
\]

To evaluate the importance of the terms in (1) we notice that \( F_{\text{AFM}} = k\Delta z \), and if the cantilever deflection \( \Delta z = 5 \text{ nm} \) and the cantilever spring constant \( k = 0.08 \text{ nN/nm} \), we get \( F_{\text{AFM}} = 0.40 \text{ nN} \). Applying \( r_t = 10 \text{ nm} \), \( \cos \alpha = 0.5 \) and \( \gamma = 0.07 \text{ N/m} \), we get \( r_t \cos \alpha / r_v + \cos(\alpha + \theta) = 0.20 \). For cases where \( r_t / r_v < 1 \), and if tip-void contact is to occur on the tip apex, it is therefore required that \( \alpha + \theta < \pi/2 \), i.e. the tip should be hydrophilic and of a small half cone angle \( \alpha_t \).

The height of a void recorded by contact mode AFM is not the height of the undisturbed void, but one that is too small by at least (see Figure 1)

\[
\Delta h = r_t (1 - \sin \alpha).
\]

Thus, knowledge of the force dependent parameter \( \alpha \) is a first requirement to determine the true height by contact mode imaging. This is difficult, but as we shall see, it can instead be found by means of force spectroscopy.

The above theoretical approach has not included the possibility that the locus of contact moves up along the tip cone. This will augment \( (F_{\text{AFM}}) \) by increasing the circumference of the locus of contact as well as \( F_p \), and thus the possibility of obtaining force balance. However, simultaneously it increases the error \( \Delta h \) of the void height measurement, and this reduces the minimum size of the interfacial voids that can be detected.

**IMAGING EXPERIMENTS**

The present experiments were performed with a Nanoscope ® Multimode™ III Scanning Probe Microscope (Digital Instruments, USA). Standard contact mode silicon AFM probes with a force constant of between 0.03 and 0.08 nN/nm, and with a nominal resonance frequency of between 10 and 20 kHz were used. The height of the probe tip was 15 to 20 µm, the nominal radius of curvature of the tip apex was \( r_t \approx 10 \text{ nm} \), and its half cone angle \( \alpha_t \approx 10^\circ \) [20]. For AFM imaging a scanning speed of typically 8 µm/s along the fast scan axis was used. Data analysis was performed using the SPIP software package (Image Metrology ApS, Denmark).

The specimens used were prepared by evaporation and vacuum deposition of gold onto substrates of mica. Thus, except for minor defects, the specimens were covered with gold crystals of a thickness of \( \sim 150 \text{ nm} \), each expected to have a (1,1,1)-surface structure, and forming an irregular pattern of grains with sizes of \( 0.2-2 \mu \text{m} \). Scanning electron microscopy (SEM) pictures (imaging in vacuum) show this structure, Figure 2a, and reveal uniformly distributed dark spots that are pits in the grain surfaces or between them. The grains exhibit surface areas that are atomically flat, and during deposition the atomic layers grow from their boundaries, while new layers develop from nucleation sites on the layers already deposited. In air AFM contact mode imaging also reveals the grain structure, and shows the difference of levels between the grains as well as holes and defects of the crystal alignment, Figure 2b. Thus, the specimens have surface irregularities, which may support the formation of interfacial voids [7].

When these specimens were investigated by AFM contact mode imaging in pure water, images as the one shown in Figure 3a1 were obtained when the setpoint of the microscope was adjusted to give the lowest possible scanning force without losing contact with the sample. The bright domains represent areas of increased height. The line scan shown in Figure 3a2 passes through four of the largest bright domains of Figure 3a1, where the line is marked. The bright domains are seen to have diameters of up to about 100 nm while their recorded heights are less than 2 nm. When the scanning force was increased, almost all the bright domains disappeared, or were transformed into smaller and darker domains, i.e. the surface bumps essentially
disappeared, Figures 3b₁ and 3b₂. When finally the scanning force was again reduced to approximately the value used for Figure 3a, the bright domains re-appeared with essentially the same sizes and heights and at the same positions as in Figure 3a. This is apparent from Figure 3c. The disappearance of the bright spots at increase of the scanning force shows that these spots were not caused by the gold surface itself. Their re-appearance without change of position at force reduction indicates that they were not due to loose, solid particles on the gold surface either. In most cases, loose particles would be pushed away from the scanned area and deposited at its boundaries, or they would move to new positions within the scanned area. This was not observed. However, the observations comply precisely with the effects expected from interfacial nanovoids. Further, a deep groove – probably between grain boundaries - is visible in the left half of the images. This groove is much deeper in Figure 3b₁ than in Figure 3a₁, and in Figure 3c₁ its depth is again strongly reduced along most of its extension. This is also evident from the line scans, Figures 3a₂, 3b₂ and 3c₂. We conclude that a long gas pocket was trapped in the groove. At increase of the scanning force, the void was penetrated, and when the force was again reduced it re-established itself with only minor changes. Before as well as after obtaining each of the images presented in Figures 3a, b and c, force curves were obtained to estimate the scanning forces applied in the three imaging cases.

**AFM FORCE SPECTROSCOPY**

In AFM force spectroscopy, the tip is horizontally stationary, while the cantilever base and the specimen are made to approach and retract from each other at constant speed. The z-motion starts from a distance of no tip-surface interaction (no cantilever deflection and \( F_{AFM} = 0 \)) and continues until shortly after the cantilever is upwardly deflected due to tip-specimen contact. This process is subsequently reversed. The cantilever deflection (which is proportional to the force of deflection) is recorded as a function of the z-position of the cantilever (base) relative to the specimen surface during their approach and retraction.

In Figure 4a such a force spectroscopy is shown for an air-solid interface. When the tip is at a distance of a few nanometer from the solid surface, attraction forces cause an accelerated snap-in of the tip, i.e. an abrupt downward (negative) tip deflection until it impacts the specimen surface. Adsorbed layers of water generally increase the snap-in distance, because an attractive surface tension force is set up when these layers get into contact. With the tip standing firmly on the specimen surface, the continued approach of the cantilever base now changes the deflection of the cantilever in a linear upward direction (proportional to the change of the specimen-cantilever distance). The snap-in distance is determined as the difference of the z-position of the cantilever at snap-in, and its position when 0-deflection is again achieved on the linear deflection curve for tip-specimen contact. During the subsequent retraction, the linear deflection curve is reversed, but it is extended beyond the point of snap-in, partly due to the tip-specimen attraction being at its maximum at contact, partly because of the merged layers of water adsorbed to the tip and the specimen surfaces. The surface tension force, which they set up, also dominates the effect of the tensile stress in the liquid, caused by the surface curvature of the liquid film. When the upwardly directed \( F_{AFM} \) becomes large enough, the liquid film breaks, an abrupt snap-out occurs, and the cantilever returns to its non-deflected state.

If the approach takes place at a water-solid interface, the same sequence of events occurs. However, during merging no liquid-gas surface exists between the tip and the specimen. The orderly structured layers of liquid, present at both the tip and the specimen surfaces, cause a tensile stress in the liquid of the tip-specimen gap, but while the gap is open, it is of minor importance only. Further, the molecular attraction between the tip and specimen is shielded by the water molecules. Therefore, the snap-in is much weaker than in air – or it is absent. After the tip-specimen contact, the highly curved interfacial layer of water around the point of contact probably leads to the formation of a vapour cavity surrounding this region, i.e. a surface tension governed tip-specimen binding force arises. This allows the tip to lose hard-wall contact with the specimen before snap-out occurs, and it is seen in the spectroscopy by the force curve ceasing to be linear prior to snap-out. Depending on the tip and specimen materials and their surface configurations, the cavity, and thus also the surface tension force, may grow more or less.
During the retraction the upwardly directed $F_{AFM}$ caused by the bent cantilever is balanced by the downwards directed surface tension force ($F_{st}$), at the locus of tip-void contact. At first, these forces grow by an increase of the vertical component of the surface tension force. However, the circumference of the locus of contact also shrinks, as the tip retracts from the cavity, and eventually ($F_{st}$) reaches a maximum, which is followed by a snap-out. The contraction of the locus of void-tip contact may take place through minor, abrupt re-organisations that result in a stepwise snap-out. This is illustrated in Figure 4b.

Using force spectroscopy in water at a position where a gaseous interfacial void exists, the topology of the void surface is changed when the tip establishes contact and sets up a new inner void boundary. To achieve force balance, the initial point contact shifts into a closed-loop locus of contact. With a weakly hydrophilic or hydrophobic tip of large cone angle causing $\alpha_o + \theta > \pi/2$, the vertical component of the surface tension force on the tip, ($F_{st}$), is downwards directed. Therefore, the tip is pulled into the void, and an upwardly directed (negative) $F_{AFM}$ builds up while the locus of tip-void contact moves up along the tip cone during the snap-in. At voids of small height, hard-wall tip contact with the specimen surface is established immediately. At large ones, a deflection enhancing force balance may be reached before impact. Thus, the continued specimen-cantilever approach leads to tip-specimen contact at maximum negative cantilever deflection, and now the deflection curve rises linearly. This precisely explains the results of Mortensen et al [1], who measured snap-in events of up to $\sim 60$ nm on a stainless steel surface by the use of Si$_3$N$_4$ tips of $\alpha_o = 35^\circ$, and interpreted these to be caused by interfacial voids of that height, Figure 4c. At retraction, the full penetration of the tip into the resulted in a very strong ($F_{s}$), which had to be overcome by $F_{AFM}$ before snap-out occurred, i.e. it was highly delayed, and went to zero deflection in a single step.
Using force spectroscopy in water at a position where a gaseous interfacial void exists, and applying a slender, hydrophilic tip for the spectroscopy the condition of void imaging, \( \alpha_0 + \theta \leq \pi/2 \), can be satisfied. In this case force balance on the tip means that the vertical component of the surface tension force, \( (F_{st})_o \), is upwardly directed. This means that from the moment of initial tip-void contact, until force balance is achieved, a small snap-in may occur. After the snap-in the continued specimen-cantilever approach pushes the tip deeper into the void that carries it, and the cantilever deflection changes non-linearly from negative to positive values. Tip-specimen contact occurs at a positive cantilever deflection – a characteristic feature of the presence of an interfacial void - and at this point the deflection curve becomes linear. The curve of retraction is essentially as that of approach, although the forces due to tip-specimen contact delays its shift from linear to non-linear shape, and irreversible changes of the locus of tip-void contact during cantilever bending may also cause quantitative changes. This is all illustrated by Figure 5, which shows an example of force spectroscopy on an interfacial void of a diameter measured to be \( \sim 150 \) nm. The height of the void can be determined from the difference of the \( z \)-positions of the cantilever base relative to the specimen when the snap-in is initiated, and when the line for tip-specimen contact during approach is extrapolated to 0-deflection. In the case shown, the height of the void was about 15 nm. Likewise, the height of the void, measured by contact mode imaging, corresponds to the \( z \)-distance between the non-linear approach deflection curve and the extrapolated linear curve of deflection, measured at 0-deflection. In Figure 5 this distance is seen to be about 3 nm. During contact mode imaging, a small positive deflection is required to maintain tip-specimen contact, and in Figure 5 this force is seen to reduce the measured void height. A reduction of the depth of the snap-in increases the measured height. This seems to happen when very large voids, \( \sim 500 \) nm or more, are studied.

**Summary**

The force balance equation for AFM imaging of voids at liquid-solid interfaces requires that \( \alpha_0 + \theta \leq \pi/2 \), i.e. the tip has to be slender and hydrophilic. With silicon tips of a half cone angle of \( \alpha_0 = 10^\circ \), the imaging of voids at water-gold surfaces was possible. Nanovoids smaller than 200 nm in diameter and of a measured height less than 2 nm were recorded, as well as gas pockets in grooves. The true heights of the interfacial voids
could be determined by force spectroscopy, and were found to be notably larger than those found during contact mode imaging.

The occurrence of nanovoids at gold surfaces submerged in water is in line with results from STM investigations of other materials [9-10] and supports results of tensile strength measurements as well as theoretical work on void formation [5-7-8].

It has long been known that natural surfaces submerged in water tend to develop surface attached bubbles. Experiments have indicated that they grow from gas nuclei, the nuclei that also serve as cavitation nuclei. With AFM force spectroscopy and by contact mode imaging we are now able to identify and image at least the larger ones.

Acknowledgement
The authors thank Dr. Jette Mackintosh for assistance in preparation of the manuscript.

References