Probe damage evaluation in frequency-modulation shear-force acoustic near-field microscopy

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Abstract. Shear-force acoustic near-field microscopy (SANM) and Whispering Gallery Acoustic Sensing have recently been introduced as a tandem system to characterize the viscoelastic response of fluids confined between two solid-boundaries in relative oscillatory lateral motion. SANM uses (a) a laterally oscillating tapered probe (attached to a quartz tuning fork QTF) as one of the trapping boundaries, and (b) an acoustic sensor (attached to the other flat-substrate boundary) that independently monitors the fluid’s acoustic emission. On the other and, WGAS is another technique that uses an acoustic transducer (attached to the frame holding the probe) to monitor the probe’s lateral motion amplitude. Steps towards improving the standing of the SANM/WGAS system as a nanometrology tool include: (i) to integrate frequency modulation methods, to thus be able to discriminate the elastic from the inelastic component of the probe-fluid interactions, and (ii) evaluate the integrity and robustness of the probe to endure such surface interactions, since eventual deformation of the probe affect the reproducibility of the measurements. Here we report using the WGAS signal (or alternatively the QTF electrical response) to control the probe’s motion in frequency modulation modality. In addition, systematic evaluation of eventual probe damage (acquiring scanning electron micrograph before and after the probe exerts one approach/retraction trip to/from the substrate) are also presented. The non-monotonic behavior of the fluid’s acoustic emission (first increasing and then decreasing) as the probe approaches the sample—which occurs before the probe touches the surface, as revealed by the lack of damaged observed on the probe—constitutes one of the main findings reported here. The acoustic signal provides clues on the fluid’s dynamic response when subjected to nanoscale confinement.

1. Introduction

The dynamic behavior of confined mesoscopic fluid films displays striking properties [1-3] that often departs from classical Newtonian liquids. The relevance of confined mesoscopic fluid studies extend to technological areas like adhesion [4, 5], wetting processes [6], and interfacial friction phenomena [7]. Understanding the dynamic response of confined fluids can shed light on the dynamics of proteins’ folding/unfolding processes [8]; given the fact that proteins are often characterized by surfaces comprised of extended nonpolar regions, the aggregation and subsequent removal of water between these hydrophobic surfaces are believed to be central to their self-organization [9,10].

Current methods widely used to characterize confined fluids include the surface force apparatus [11] and atomic force microscopy (AFM) [1], in which the fluid is basically sandwiched between two solid...
boundaries (referred here as the probe and the substrate) each attached to mechanical springs. In these traditional methods the fluid’s properties are inferred from the springs reactions [1,11]. In contrast our group has recently introduced a new method, shear-force acoustic near-field microscopy (SANM) [12], where the fluid under shear is independently monitored by its acoustic emission. SANM uses a laterally oscillating tapered probe (attached to a quartz tuning fork) as one of the trapping boundaries, and an acoustic sensor in contact with the other flat-substrate boundary to—indepen dent from the probe—monitor the fluid’s dynamic response to the shear interactions (see Fig. 1a).

The ability to detect acoustic waves even when the probe is not in mechanical contact with the substrate (i.e. the sound is engendered at the mesoscopic fluid and not the result of the probe tapping onto the substrate) constitutes one of the main features of the new technique. SANM brings then a new sensing mechanism—near-field acoustic detection—to help characterizing confined fluids under shear. Herein we emphasize on SANM instrumentation improvements, namely evaluation of potential probe damage during test, and incorporating frequency modulation detection method. The latter would allow discerning elastic from inelastic components of the probe-fluid interactions.

2. Current SANM status: tests at single driving frequency
SANM uses a sturdy quartz tuning fork (QTF) [13] held by the frame of the microscope. A sharp stylus (a tapered metal wire, or the pyramid of an AFM cantilever) is attached at the bottom of one of the QTF tines (see Fig. 2), altogether constituting the probe.

In a typical test, the probe is electrically driven at its resonance frequency (10 nm amplitude, measured when the tip is far away from the substrate). While keeping this frequency constant, the probe apex is gradually brought into the proximity of the substrate. At a very close probe-sample distance (which varies stochastically, from few nm to tens of nm, depending on the surfaces wetting properties, the environmental humidity, and the temperature) a water meniscus is suddenly formed [14] (figure 1, on the left side); this
gives rise to the emission of an acoustic signal, as well as to a decrease in the probe’s amplitude. Both signals vary with the probe-sample distance, as well as whether the probe is advancing or retracting from the substrate. Fig. 1 (on the center) shows a typical retraction trace. Through a linear model of the probe’s motion (the QTF tine is typically modelled as a mechanical simple harmonic oscillator) the elastic and damping properties of the fluid are inferred [7,15]. In the new SANM, the fact that the fluid’s properties are inferred directly from its acoustic emission—and not indirectly inferred from the probe’s motion—shall contribute to a better understanding of these mesoscopic systems.

A shortcoming of measurements performed at constant driving frequency is that a decrease in the probe’s oscillation amplitude (as observed when the probe-substrate distance decreases) is actually caused by two factors: the damping forces and the “blue” shift in the probe’s resonance frequency. Such a frequency shift is also reflected in the acoustic signal, as seen in Fig. 1 (on the right side). Hence, a decrease in the probe’s amplitude is not an exclusive signature of a damping force. It would be ideal to discriminate the damping and elastic components of the intervening solid-fluid interactions. One option is to use Phase Lock Loop (PLL) control feedback, which is explained below.

**Figure 2.** Phase-locked-loop (PLL) feedback-control integrated to the WGAS/SANM system to discriminate the damping from the elastic components of the probe-fluid-substrate interactions. The control signal can be set to be given by either the QTF electrical response (switch at position-1) or to the WGAS signal (switch at position -2 and placing point 1 to ground.) The QTF is attached to the frame of the microscope (dashed lines cylinder). The substrate (attached to an acoustic transducer) rest on a z-piezo scanner, which establishes its vertical position. Once the water bridge meniscus is formed, the probe’s resonance frequency changes as the probe-substrate distance decreases; the PPL system responds by driving the QTF \( V_{\text{drive}} \) at its new resonance frequency. Accordingly, during an approach/retraction process, the probe is always oscillating at resonance condition. A decrease in the lateral oscillation amplitude can then be attributed solely to damping component and the frequency shift to elastic component of the probe-fluid-substrate interaction.
3. Operation with phase lock loop (PLL) control feedback using either WGAS or QTF signal

Figure 2 shows schematically an adaptation of the PLL feedback control [16] built into our WGAS/SANM system. The QTF (with a sharp stylus attached to one of its tines) is electrically driven at its resonance frequency (~ 32 kHz, 10 nm amplitude). At resonance conditions \( i \) with the switch in position-1, the QTF electrical sinusoidal signal response is in phase with respect to the sinusoidal driving voltage \( V_{\text{drive}} \). Alternatively \( ii \) with the switch in position-2, the whispering-gallery acoustic signal (WGAS) can also be used; WGAS, another acoustic base sensing mechanism recently developed in our lab [17], offers an alternative way to more accurately monitor the QTF mechanical oscillations (the QTF electrical response which not always correlates with the QTF mechanical response [16]).

During a probe approach, once the apex starts interacting with a mesoscopic fluid (assumed viscoelastic), the QTF mechanical response undergoes a phase change because it is now out of resonance. Such a change in phase (detected electrically by the QTF or the WGAS sensor) is utilized by the PLL section of the circuit (sitch in position 1 or position-2), where a voltage controlled oscillator (VCO) responds by adjusting the frequency \( \omega \) of the driving voltage \( V_{\text{out}} \) until the laterally oscillating probe reaches again resonance condition (i.e. the phase of the signal at pin #1 or pin #2 is back in phase with the driving voltage) at the new probe-sample distance. This way, \( i \) changes in the probe’s amplitude can be ascribed to damping effects; and \( ii \) the change in the resonance frequency gives a direct measurement of the elastic component of the probe-fluid interaction.

4. Implementation

Fig. 3 shows schematically the WGAS/SANM experimental setup. Subsections of its implementation are described next.

![Figure 3. Block diagram of the WGAS/SANM experimental arrangement.](image-url)
4.1 Piranha cleaned sample
A substrate with hydrophilic characteristics was prepared by cleaving a 1 cm square section of silicon wafer with its native oxide intact. The substrate was first ultrasonically cleaned in a solvent bath of acetone for 15 minutes to remove particulates and oils from the surface. It was then rinsed thoroughly in deionized water before soaking for 30 minutes in a Piranha etch solution. Cleaning procedure with piranha solution is expected to renders OH groups thus giving the surface a hydrophilic character [18]. Piranha is composed of three parts of concentrated sulfuric acid and one part of 9.8M hydrogen peroxide, which removes any remaining organic matter on the surface of the substrate. It is worth noting that great care must be taken when adding the hydrogen peroxide to the sulfuric acid; it must be done drop by drop, as the reaction is extremely exothermic. Finally, the sample was rinsed again with deionized water, and a ~20° water contact angle was verified.

4.2 Fabrication of Gold Tapered Probes
The SANM sensor comprises a tapered probe adhered to a quartz tuning fork (QTF). Alternative to attaching an AFM cantilever (although also used herein), a more economical option is in-lab fabrication of tapered metal wires. As starting material, we used gold wire of 125 µm diameter (99.95% purity). A 4 cm long segment of gold wire was connected to an anode contact, oriented vertically, and positioned in such a way that 5 mm of the wire protrudes below the edge of the plate holder station. An etching solution consisting of one part hydrochloric acid at 37% concentration, and one part ethanol at 95% purity grade was placed in a small beaker below the gold wire. A 3-cm long, 1/8” diameter, graphite rod was used as the cathode. Bubbles are created around the cathode during the etching process; as they rise and break near the surface of the solution, they have a detrimentally effects on the roughness of the probe and, eventually, on the probe’s apex. To prevent this adverse effect, a plastic pipette (trimmed into a cylindrical shape) is placed concentrically over the cathode. This cover guides the bubbles up through the inside of the pipette walls, so that they can be vented. To generate the etching current, an ac voltage (2 Volts amplitude, 150 Hz) plus a 2 Volts dc bias was applied between the gold wire and the graphite cathode. The z axis positioner was lowered until approximately 2 mm of the gold wire is submerged, and a 25 mA peak-to-peak current is measured. After approximately 90 seconds, the etching current drops to zero, at which point the z positioner is abruptly raised. The gold wire is then removed and rinsed in acetone bath. Finally, the etched portion is cut from the remaining gold wire yielding a tapered probe approximately 700 µm in length, which is subsequently attached to a quartz tuning fork using minimal amount of epoxy glue.

4.3 Humidity chamber
Depending on the wetting properties of the probe and substrate, as well as the humidity and temperature of the surrounding environment, a water meniscus is suddenly formed when the probe apex is placed in the proximity of the substrate. To increase the probability of water meniscus formation in our measurements, an acrylic chamber was built to enclose the microscope head-stage, and establish relative humidity (RH) above the typical 35% existent in our lab ambient. The RH is established through a combination of i) injecting low pressure humidified air, and ii) placing inside the chamber a saturated salt solution. A Kestrel 4200 flow tracker monitors the humidity in real time. Low-pressure humidified air was created by first sending compressed air (regulated at 0.5 psi) through a tubing network, then through a humidifier, and finally injecting the vapor stream into the chamber through an open cell foam diffuser. The humidifier comprises a stoppered 1L Erlenmeyer flask containing deionized water and two tubes, one bubbling air through a ceramic stone and the other returning the humidified air to the chamber. On the other hand, a saturated sodium bromide solution was placed in a shallow watch glass (a round, concave glass dish used for evaporation in chemistry) inside the chamber to exploit its fixed-point humidity of 59.1% at 20 °C.
Employing concurrently both methods allows bringing the chamber to a RH dictated by the selected saturated salt solution.

4.4 Estimation of the probe’s oscillation amplitude

Based on previous calculations [12], the QTF have an electro-mechanical coupling constant of 0.4 nA/nm. Upon acquiring a spectral response, the difference $\Delta f$ between the current measured at resonance and the one measured well off resonance allows estimating the probe’s amplitude. In this experiment, for 70 mV driving voltage one measures $\Delta f = 23$ nA, which gives an estimated value of 9 nm amplitude of oscillation.

5. Experimental results

5.1 SANM operation in frequency modulation mode and using an AFM/QTF probe

For these tests an AFM cantilever was glued to the bottom of one of the tines of a quartz tuning fork (520-TFC3X8-X, Mouser Electronics) of dimensions in length $L=3.8$ mm, thickness $t=0.6$ mm, and width $w=0.35$ mm. Modelling the tine of a QTF as a harmonic oscillator gives an effective spring constant $K=\left(\frac{E}{4}\right)\frac{w}{(t/L)^3}=26\times10^3$ N/m, and a piezoelectromechanical coupling constant $\kappa=6.5\times10^{-6}$ C/m. Here we just exploit the pyramid of the AFM cantilever, hence any type of commercially available cantilevers would work fine.

Figure 4 demonstrates the operation of SANM in frequency modulation mode, the latter outlined in Section 3 above. The experiments were carried out at 43% relative humidity. The probe performs an approach/retraction test at 2 nm/s. The sample is a silicon sample covered on top with a monolayer of hydrophilic Poly(2-ethyl-2-oxazoline) (PEOX); 35º contact angle. The probe’s amplitude (monitored by the QTF and WGAS signals), the resonance frequency shift (tracked by the PLL feedback electronics), and the acoustic emission from the fluid (SANM signal) are all simultaneously measured. Here we highlight the robustness and integrity of the probe, as revealed by the SEM micrographs Figure 4d. The SEM images of the probe were taken before and after the approach/retraction process; notice the shape of the pyramid appear intact in the images. This shows evidence that, while acquiring the traces displayed in figures 4 a-c, the probe has not been in mechanically contact with the substrate.

Succinctly, figure 4a indicates the resonance frequency shift is of the order of a few Hz. Figures 4a and 4b show the similarity between the electrical-QTF and acoustic-WGAS signals; this encourages to keep improving the sensitivity of the acoustic-based WGAS signal detection (and eventually replace the electrical-QTF detection) given its more direct correlation with the actual mechanical motion of the QTF probe [17]. Figure 4c is quite revealing; it displays a close correlation between the fluid’s near-field acoustic emission and the probe’s resonance frequency shift (in the region where the acoustic signal monotonicely increases during the approach.) Interpretation of acoustic emission as an elastic energy dissipation channel in interfacial interactions is reinforced by these measurements, which should have implications in nanotribology studies [19]. Admittedly, Figure 4c also indicates that such a correlation breaks down at shorter probe-substrate distances, where the SANM signal decreases while the frequency-shift keeps increasing as the probe-substrate distance decreases. A couple of plausible arguments can explain this result: On one hand, the decrease in the acoustic signal may be a consequence that the fluid, trapped between the probe and the substrate and initially resilient to remain stuck to the solid boundaries, gives up and gets quizzed laterally out by the vertically approaching probe. In that scenario, the lower the amount of trapped water, the lower the acoustic emission signal intensity. On the other hand, the fact that frequency shift keeps increasing suggests that the water layers closer to the substrate display a solid-like behavior. As complementary information that support these interpretations, our lab has observed (in other experiment not reported here) that in the region where the acoustic signal experience a peak during the approach the probe’s apex has not made mechanical contact with the substrate yet.
Figure 4. Experiment using a QTF/AFM probe and a hydrophilic polymer sample (PEOX). (a) and (b) Approach/retraction traces of the fluid acoustic emission, contrasted with the probe’s oscillation amplitude (QTF and WGAS signals respectively). (c) The fluid’s acoustic emission (SANM) compared with the probe’s resonance frequency shift. (d) SEM micrographs of the probe acquired before and after the approach/retraction; no permanent deformation of the probe is observed. Scale bar is 15 μm.

5.2 Testing the integrity of tapered gold probes
In this section we use a tapered gold tip attached to one of the tines of a QTF. The sample is a hydrophobic silicon wafer, whose native oxide was removed by immersion in a dilute HF solution (1.5% in H₂O) for 15 min at room temperature following Piranha cleaning described above (this latter step is optional). This procedure gives a surface of hydrophobic character; approximately 90° contact angle.

The SANM is operated in PLL modality. When the tip is far away from the surface, the resonance oscillation amplitude is 9 nm. The tripod-like microscope head-stage (which houses the probe) is lowered
first through a coarse approach procedure, using three fine-thread screws activated with stepper motors; this way the tip is positioned down to approximately 20 µm distant from the sample. Subsequently, a fine approach (at 10 nm/s) is performed by up lifting the sample stage, which is implemented with a piezo stage (MCL Nano-Z50HS). The piezo controller operates in closed loop PLL feedback (to keep the probe in resonance at all times). The approach proceeds until the probe’s amplitude (QTF signal) drops below two times the noise level of the detection system. This decrease in amplitude is indicative of interaction forces between the probe and the sample (more likely, between the tip and the incipient formation of a water meniscus); the probe is then immediately retracted until it just breaks away from any water bridge. Subsequently, a renewed fine approach starts but at lower speed (2 nm/s) until the amplitude decreases to a predetermined percent set point (90%, 80%, or 60%); upon reaching the particular set point, the probe is retracted at 2 nm/s. The approach/retraction process, with the same set point, is repeated 3 times, to verify reproducibility. Then the probe is removed for SEM imaging and evaluation of the probe’s integrity. The full process is repeated for each selected amplitude decrease set point.

Figure 5. Left: SEM micrographs of a pristine gold probe. Right: The same probe after approaching the sample until its resonance amplitude decreases to 90%. Scale bar is 8.5 µm.

Figure 5 (on the left side) shows a SEM micrograph (15 kV accelerating voltage and 10 µA emission current) of a pristine gold probe. The probe is loaded into the SANM system and driven at its resonance frequency with 9 nm amplitude of oscillations. The integrity of the probe’s morphology is tested by approaching the tip towards the sample until the QTF amplitude decreases to 90% (following the procedure described in the previous paragraph. i.e. fast approach/retraction first, then a slow approach/retraction, while the PLL feedback updates the probe’s resonance frequency at all times.) An image of probe after this process is shown in figure 5 (on the right side), which verifies the probe’s apex has experienced no damaged.

The procedure followed here (moving the probe back and forth between the SANM stage and the SEM system) is not exempt of accidental crashes of the tip. This eventuality may occur also during the initial fast approach rate (10 nm/s) included in the protocol (for the probe to find the substrate.) This is more problematic when testing hydrophilic samples, since, as seen in other tests in our laboratory, the meniscus formation occurs at shorter distance from hydrophilic substrates (compared to hydrophobic samples). Whatever the origin, we did verify deformation of the tip in one of the tests. But, when proceeding with the tests, we verify again that the tip morphology does not deform (see figure 6) when the probe approaches the sample until its resonant amplitude decreases to 60%.
6. Conclusions
Frequency modulation (phase-lock-loop feedback) was successfully implemented into Shear-force Acoustic Near-field Microscopy. The ability to discern the elastic and inelastic components intervening in probe-fluid interaction enhances the versatility of the new acoustic technique to study the dynamic behavior of confined fluids under shear. Tests on the integrity of the probe (whether they undergo deformation or not after approaching the sample) suggest that AFM/QTF are very robust. Tests with gold probes needs further tests for a more definite conclusion, still two cases were presented where the probe remained intact after the probe’s resonant amplitude decreased down to 90% and 60% of its initial resonance amplitude (the latter measured with the tip placed far away from the substrate). PLL/SANM using AFM/QTF probes revealed that the SANM acoustic signal provides more information than the monotonic-decreasing behavior of the probe’s amplitude of lateral oscillations, as the probe approaches the sample. The acoustic signal, first increasing and then decreasing, suggest a following plausible dynamic behavior of the fluid at different stages of confinement: a fluid that is initially resilient to remain adsorbed to the substrate despite the shear motion of the upcoming probe (and thus being able to emit sound), but then being squeezed out of its confinement (at the final stages of the approach) due to the hard compression exerted by the approaching probe (hence, the less amount of water, the lower the intensity of the acoustic emission.) The solid like behavior of the fluid at small probe-sample distance (as revealed in the SANM by the monotonic increase in the probe’s resonance frequency shift) offers an opportunity to test the behavior of fluids containing just few adsorbed monolayers.

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