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Using the quartz crystal microbalance to study macro- and nanoscale bubbles at solid-liquid interfaces

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Abstract. We show here that macro- and nanoscale bubbles can be detected by Quartz Crystal Microbalances (QCM) submerged in liquids. QCM’s are high quality factor oscillators that generate a shear wave when submerged in a fluid. The damping of the oscillation by the fluid causes the resonance frequency of the QCM to shift, and a viscosity can be calculated from the frequency shift. Since the shear wave generated is so short, this is a near-surface viscosity as opposed to a bulk viscosity. When bubbles cling to the QCM face the viscosity of the liquid as measured by the QCM will be reduced from the true bulk viscosity of the liquid. In this study we have submerged QCM’s with both hydrophilic (gold or silicon dioxide) and hydrophobic (octadecanethiol) surfaces in water distilled to varying degrees, including seltzer water and vacuum distilled DI water. The seltzer water has visible macroscale bubbles, and so we were able to correlate video acquired of the QCM submerged in the seltzer water with the viscosity data to directly link the presence or absence of a bubble to a change in the measured viscosity.

Recently, there has been much interest in the presence of so-called nanobubbles on solid surfaces submerged in liquids. Nanobubbles have been imaged by scanning probe microscopy [1], and the effects of nanobubbles have also been seen in the surface forces apparatus, which measures small surface forces [2]. We show here that the presence of nanobubbles can also be detected by Quartz Crystal Microbalances (QCM) submerged in liquids. QCM’s are high quality factor oscillators, and the QCM’s used in this study oscillate transversely at frequencies of 5 MHz. When submerged in a liquid a QCM will set up a transverse shear wave in the liquid. This shear wave is heavily damped, with decay lengths [3] given by:

\[ L_d = \left( \frac{2\eta_L}{\rho_L\omega_s} \right)^{1/2} \]  

(1)

Here, \( L_d \) is the decay length, \( \eta_L \) is the liquid viscosity, \( \rho_L \) is the density of the liquid, and \( \omega_s \) is the angular frequency at series resonance. In water at room temperature the decay length for a 5 MHz QCM is approximately 250 nm. The short decay lengths of the shear wave make the QCM very sensitive to small near-surface phenomena such as nanobubbles. QCM’s in liquids can be used to measure the viscosity of the liquid, as given by the Kanazawa equation [3]:
\[ \Delta f = -f_q \gamma_\frac{1}{2} \left( \frac{\eta_L \rho_L}{\pi \mu_q \rho_q} \right)^{\frac{1}{2}} \]  

(2)

Here, \( \Delta f \) is the frequency shift, \( f_q \) is the resonant frequency of the quartz prior to immersion in liquid, \( \mu_q \) is 2.947 x 10^{10} \text{ Pa} is the shear modulus of quartz, and \( \rho_q \) is 2.648 x 10^3 \text{ kg/m}^3, the density of quartz. Because the shear wave generated is so short, this is a near-surface viscosity as opposed to a bulk viscosity. When bubbles cling to the QCM face the viscosity of the liquid as measured by the QCM will be reduced from the true bulk viscosity of the liquid.

Previous studies have shown that nanobubbles form in water when the solid surface is hydrophobic, but not when the solid surface is hydrophilic. [1,2] In this study, we have submerged QCM’s with both hydrophilic (gold or silicon dioxide) and hydrophobic (octadecanethiol on gold) surfaces in water distilled to varying degrees, including seltzer water, sonicated DI water, and vacuum distilled DI water. For our studies of a hydrophilic interface we used 5 MHz AT-cut quartz crystals purchased from Maxtek with gold electrodes and gold electrodes coated with SiO_{2} overlayer. For our hydrophobic interface we used 5 MHz AT-cut quartz crystals purchased from Maxtek with gold electrodes and then used standard techniques [4] to apply octadecanethiol (C-18 thiol) self assembling monolayer (SAM) coatings.

In this study we used a Maxtek Research Quartz Crystal Microbalance (RQCM) system. To measure the near-surface viscosity of a liquid we first tuned the crystal in air and took data for approximately five minutes with the crystal in air to allow for an accurate reading of the crystal’s resonance frequency. With this resonance frequency as our reference point, we then submerged the crystal in the liquid, retuned the crystal in its new environment, and observed the shifts in the crystal’s resonance frequency with time. We used this frequency shift to calculate our near-surface viscosity, according to Eq. 2. Since our RQCM system is multi-channel, we were able to take data using hydrophilic and hydrophobic QCM surfaces simultaneously. Data runs lasted up to 24 hours. During each data run the temperature was monitored using a k-type thermocouple interfaced with the RQCM system.

The seltzer water has visible, macroscale bubbles, so we were able to correlate video acquired of the QCM submerged in the seltzer water with the viscosity data to directly link the presence or absence of a bubble to a change in the measured viscosity. See figure 1 for snapshots from this video. In figure 1a an arrow indicates the presence of a large bubble on the QCM SAM surface. At this point the near-surface viscosity is measured as 0.66 cP, as can be seen in figure 1c. (The errors in the viscosity measurements for this crystal are approximately 1\%.) Figure 1b shows the the QCM SAM surface one second later; after the bubble has moved off of the surface. In figure 1c this corresponds to a near surface viscosity of 0.92 cP.

For the seltzer water, data was acquired for two hours after the seltzer water was decanted with both gold (hydrophilic) and octadecanethiol (hydrophobic) QCM surfaces. This data is shown in figure 2. For the first hour after decanting for the SAM crystal, the viscosity is quite erratic. This is due to bubbles continuously forming on the SAM surface and then either popping or moving off or across this surface. As time goes on, the viscosity curve as measured by the SAM crystal becomes smoother and approaches a limiting value of 0.0009 Ns/m^2. This is because the carbon dioxide gas leaves the solution as time increases and the seltzer water “goes flat.” This clearly shows the dependence of the measured viscosity on bubble coverage. In the beginning, bubbles cover more of the QCM surface, which results in a lower time-averaged near-surface viscosity. As the seltzer water goes flat, fewer bubbles are available, coverage is lower, and therefore the
The time-averaged measured viscosity is higher. For the hydrophilic gold surface, however, the seltzer water viscosity curve was quite stable. As shown on the video, bubbles simply did not form on the QCM surface after several minutes of immersion in the seltzer water.

Figure 1. Snapshots made before (1A) and after (1B) a large bubble moves off of the QCM face. Figure 1C depicts the viscosity vs. time, and the arrow indicates the jump in viscosity due to the bubble in 1A moving off of the face.

Figure 2. Near-surface viscosity of seltzer water vs. time after decanting for the hydrophilic gold crystal (top, dashed curve) and the hydrophobic SAM crystal (lower, solid curve).
We thermally distilled water by attaching an isolatable reservoir filled with DI water to our multi-purpose vacuum chamber. The water was first frozen with liquid nitrogen, then any excess vapor was pumped off of the frozen sample, and finally the water was then thawed. This process was repeated until the vapor pressure of the sample in a frozen state was less than 0.01 mbar. Then vacuum was broken, and the viscosity measurements were carried out at atmospheric pressures simultaneously for both hydrophilic and hydrophobic QCM surfaces for two weeks. Each viscosity data set was acquired over a period of 24 hours. At the end of the 24 hour period, the 20 minutes of viscosity data were averaged to obtain the measured near-surface viscosity. Figure 3 shows the near-surface viscosities for the water as measured by the hydrophobic SAM crystal over the two week period, and also gives the known bulk viscosity of water at the temperature of the water on that day.

Several interesting points can be seen in figure 3. First, note that the near-surface viscosity of water as measured by the hydrophobic crystal is lower than the bulk viscosity of water for the entire two week period, indicating the presence of nanobubbles at the solid-liquid interface. Also note that for the first week of sitting in ambient pressures the near-surface viscosity as measured by the hydrophobic crystal remains relatively constant. After the first week, however, the near-surface viscosity measured by the hydrophobic crystal begins to drop even further away from the known bulk viscosity of water. This indicates greater coverage of nanobubbles on the solid-liquid interface as time increases. This is most likely due to the diffusion of air back into the distilled water with increasing time post-distillation.

![Figure 3. In circles, the viscosity of the distilled DI water as measured by the SAM crystal vs. time from breaking vacuum in days. The squares represent the known bulk viscosity of water at the measured temperature.](image)

**References:**


