Characterizing Evaporation of a Sessile Droplet using Quartz Crystal Microbalance

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Abstract – In this work, the interaction between a quartz crystal microbalance (QCM) and an evaporating sessile droplet is elucidated. Specifically, we differentiate the QCM response to changes in the interfacial contact area and the dynamic contact angle. This is carried out by developing a computational model combining the electrical and structural analysis of quartz with the thermo-viscous behavior of a sessile droplet. From our computational model we conclude that a change in contact angle alone has negligible effect on the frequency response of the QCM. On the other hand, a change in the interfacial contact area of an evaporating droplet has a significant effect on the frequency response of the QCM.

1. Background

Evaporation is important in several applications as diverse as inkjet printing, spray cooling, micro and nanoscale fabrication [1]. As a result, it has been the subject of much investigation. One of the techniques used to study evaporation on different surfaces involves monitoring the change in mass of a sessile droplet. In this regard, the use of a quartz crystal microbalance (QCM) as an ultrasensitive mass sensor can be a viable approach [2]. QCMs are piezoelectric oscillators that generate a bulk acoustic wave across their thickness when operated with an alternating voltage close to their resonant frequency. A change in the resonant frequency due to a change in the loading of the QCM allows for accurate measurements of any variation in the mass located on the QCM. Consequently, several research efforts have leveraged this feature to study evaporation of sessile droplets.

Joyce et al. used QCM to study evaporation of a homologous series of alcohols. In this study, the authors claim to have observed different modes of droplet evaporation associated with constant contact area and constant contact angle [2]. Similarly, the various stages of evaporation noted by Picknett and Bexon [3], and described by Bourgès-Monnier and Shanahan [4], were perceptible in the frequency response of the QCM. More recently, Couturier et al. concluded that the frequency response from an evaporating sessile droplet is related to the edge of the droplet [5]. Specifically, they demonstrated that evaporation with a constant contact area can also result in a small but perceptible frequency change [5]. On the contrary, Pham and coauthors, who used QCM to study the interfacial effects of drying colloidal suspensions, noticed that a rough QCM showed no change in resonant frequency during the constant contact area stage of evaporation [6]. Similarly, Lin and Ward showed that sessile droplets on a QCM give a response corresponding to the contact area [7]. In summary, a review of prior work indicates that while evaporation of sessile droplets has often been analyzed using the QCM, a conclusive relationship between the dynamic contact angle and QCM response is not available. In the present work, we address this by studying the interaction between the QCM and the sessile droplet for different contact angles using computational modeling.

2. Computational Modelling of QCM Response

The fully coupled dynamic model of a piezoelectric AT-cut QCM with a sessile droplet is governed by the coupling of Hooke’s law and Maxwell’s equation in the piezoelectric domain, and by Navier-Stokes equation in the fluid domain. The constitutive equations for the piezoelectric quartz are given by Eqn. 1. Here \( T \) is the stress, \( S \) is strain, \( E \) is electric field and \( D \) is electric displacement. The material property matrices, \( s^{\|e} \), \( d \), and \( e^\| \) describe the compliance at constant electric field, piezoelectric constant, and permittivity of quartz at constant strain [8].

\[
\begin{bmatrix}
\sigma \\
\text{d} \\
e^\| 
\end{bmatrix} =
\begin{bmatrix}
s^{\|e} & d \\
& e^\| 
\end{bmatrix}
\begin{bmatrix}
T 
\end{bmatrix}
\]

(1)

These properties depend not only on the material, but also the crystallographic plane on which the crystal is cut. In this study, an AT-cut crystal was studied, as illustrated in Fig. 1. The quartz crystal is 16.635 \( \mu \)m in thickness and 14 mm in diameter with concentric electrodes of radius 5 mm.

![Figure 1. Cross section and top views of QCM with a centrally placed sessile droplet. The computational study of QCM response considers an AT-cut quartz crystal, coated with concentric electrodes on both sides, with a centrally-placed water droplet](image)

The electrical boundary conditions applied on the piezoelectric domain are a sinusoidal voltage on the non-sensing (bottom) electrode and ground on the sensing (top) electrode. The solid and fluid domains are coupled by continuity in velocity. The solid-fluid interface and the fluid domain are all considered isothermal. Additionally, the pressure at the droplet surface is given by the Laplace pressure based on its curvature. The governing equations are then applied to a meshed geometry and solved in the frequency domain over a range of applied voltage frequency to find the resonant frequency.

For the chosen material constants, the fully coupled dynamic model shows that the QCM will oscillate in a thickness-shear mode along the x-axis (see Fig. 1). Viscoelastic coupling between a fluid and the QCM will decrease the resonant frequency as a function of density, \( \rho \), and viscosity, \( \mu \) [9, 10]. As the quartz crystal oscillates due to the applied voltage, it drags a layer of fluid in phase with it but the velocity of this layer decays as the distance from the surface increases [10, 11]. The effective height of this layer determines the amount of frequency shift, which is related to the kinematic viscosity and frequency of the QCM. This quantity is termed the viscous decay length, \( \delta \), and is given by Eqn. 2. For water on a 10 MHz quartz crystal \( \delta \approx 170 \text{ nm} \). The shear waves from the QCM will decay to \( e^{-\delta} \) of their original magnitude in a distance of \( \delta \), and the mass sensing capability of the QCM is approximately \( \delta/2 \) [7].

\[
\delta = \frac{2\mu}{\sqrt{\omega \rho}}
\]

(2)

A fully coupled dynamic simulation of QCM with a droplet of 10 \( \mu \)m contact radius was performed for contact angles of 90°, 60° and 30°. To calculate the frequency response of these droplets, the frequency that gives the maximum admittance of the QCM was subtracted from the unloaded natural frequency of the crystal. It was found that the 90° droplet had a frequency shift of 4.9689 \times 10^{-2} \text{ Hz}, while the 60° droplet had a shift of 4.9682 \times 10^{-2} \text{ Hz}.
and the 30° droplet had a shift of 4.9683 × 10⁻² Hz on a QCM with natural frequency of 9.97 MHz. The fully coupled dynamic simulation shows that while the frequency response is indeed different, it may not be large enough to be perceivable experimentally for small (~10 μm) droplet. A similar comparison can also be carried out for larger droplets. However, increasing the radius greatly increases the droplet volume and a fully coupled dynamic simulation becomes computationally challenging. Therefore, to compare droplets of larger radii, the simulation must be simplified. We conducted a decoupled dynamic model considering the sessile droplet and QCM separately. The frequency response to different contact angles with similar contact area was obtained by mapping the shear stress from the droplet analysis onto the QCM surface, as described below.

In an unloaded QCM the sensing surface can be considered to be stress free, however in the case of a semi-infinite fluid, the QCM can be analyzed with an equivalent shear stress [10, 12]. For a semi-infinite fluid on an ideal QCM with a Gaussian surface velocity profile, the velocity in the fluid domain can be derived from the Navier-Stokes equations, as done by Martin and Hager [13]. The force coupling the QCM with the semi-infinite fluid is the wall shear stress given by Kanazawa [10]. From Martin and Hager’s equations, the shear stress in a semi-infinite fluid can be derived for the oscillating wall with a radially dependent velocity magnitude. Equation 3 gives the shear stress at the droplet-QCM interface, where \( T_{xz} \) is the shear stress on the fluid, \( \nu_0 \) is the maximum velocity at the center of the electrode, \( a(\pi=2) \) is a constant intrinsic to the QCM [8], \( r \) is the radial coordinate, \( r_e \) is the electrode diameter. Using \( T_{xz} \) as a boundary condition over the whole sensing surface \( (r = 0 \text{ to } r = r_e) \) of the dynamic mapped model, Kanazawa’s equation [10] can be recovered.

\[
T_{xz} = -\nu_0 \sqrt{2\mu\rho} \ e^{-ar^2/2} \cos(at + \frac{\pi}{2})
\]

(3)

The independent droplet analysis involves finite element modeling of a sessile droplet on an oscillating base. An important outcome of this analysis is the shear stress profiles, which can be mapped on to the QCM surface. As anticipated, the shear stress \( (T_{xz}) \) obtained by the droplet analysis in the region close to the center of the droplet is identical to that given by Eqn. 3. Towards the edge of the droplet, \( T_{xz} \) changes magnitude and phase, additionally, \( T_{xz} \) and \( T_{zz} \) become non-zero and of similar order of magnitude as \( T_{xz} \). This is due to all three components of velocity becoming relevant when the surface of the droplet is close to the QCM surface. From our decoupled dynamic model, it is clear that droplets of different contact angles can have different shear stress profiles near the contact line. In addition we found that the fully coupled and decoupled models yield nearly identical shear stress profiles, indicating that the decoupled modeling approach is viable.

Figure 2 shows \( T_{xz} \) at the droplet-QCM interface normalized by the stress given by Eqn. 3 along the x-axis for droplets of the same radius (10 μm) and contact angles of 90°, 60° and 30°.This deviation in \( T_{xz} \) away from the center of the droplets for different contact angles can potentially affect the frequency response of the QCM. To quantify this, \( T_{xz} \) was mapped onto the surface of the QCM. With the mapped shear forces found to be an accurate representation of a sessile droplet on a QCM, the difference in the frequency response of the two droplets of different contact angles was found to be quite small. For a 10 μm contact radius droplet that has a frequency shift of 5 × 10⁻² Hz, a change in contact angle from 90° to 60° corresponds to an increase in the resonant frequency of 7 × 10⁻² Hz. Similarly, for a larger droplet with a contact radius with a frequency shift of 459 Hz, the resonant frequency shift between two contact angles (from 90° to 60°) was found to be 8×10⁻³ Hz. In summary, for both small and large sessile droplets, the frequency change between a 90° and 60° droplet is almost inconsequential.

The frequency response observed in some evaporation experiments from changing contact angle is much larger than expected from the numerical analysis. The constant contact radius stage observed by Courrier et al. [5] for a 1.1 μL with a radius of 1 mm has a frequency response of about 10 Hz, while the total shift after droplet deposition is about 245 Hz on a 3rd order overtone order 5MHz crystal. It is possible that this frequency shift is due to a microscopic (order of 15 μm) contraction in the radius of the drop. This agrees with Courrier’s order of magnitude prediction that the relevant area is on the order of 10 μm from the edge of the droplet.

![Figure 2](image1.png)

Figure 2. Normalized shear stress at the droplet-QCM interface as function of normalized radial location for two different contact angles. Inset shows normalized shear stress across the entire droplet.

From this work we conclude that a change in the contact angle of a water droplet changes the shear stress profile at the droplet-QCM interface. However, this change in the shear stress profile is confined close to the edge of the droplet. Consequently, the frequency response of the QCM may not show a significant variation. Any perceptible changes in the frequency response during the changing contact angle phase of evaporation could in fact be due to microscopic stick-slip motion of the contact line [2, 5]. The frequency response from a purely constant contact radius mode of evaporation would not vary significantly as the contact angle changes. Using a rough QCM surface Pham et al. [6] noted that the response during evaporation was invariant. This is likely because the droplet was sufficiently pinned. Their results from a smooth crystal more closely followed Courtier’s work and those droplets were likely undergoing a mixed-mode evaporation [2].

**References**