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Dynamic Response of Quartz Crystal Microbalances in contact with Silicone Oil Droplets

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Abstract

Quartz crystal microbalances (QCMs) in contact with liquid droplets have been used to investigate the rheological properties of liquids and the diverse solid-liquid interfacial phenomena. In this article, we first report the experimental results of the QCM responses due to the deposition of microliter droplets of silicone oils. The silicone oils with viscosity in a range from 50cS to 10³cS are tested. It has been found that the responses in the frequency and resistance measurements of the QCM in contact with the silicone oils are different from the Newtonian liquids. More importantly, it has been found that for the silicone oils the frequency of the QCM steadily increases for several hours and even exceeds the initial value of the unloaded QCM which has resulted in the positive frequency changes. The collaborative effects of the interfacial slip and viscoelasticity have been discussed to qualitatively interpret the positive frequency changes. Secondly, we discuss the cyclical variations in the frequency and resistance during the experiments of the silicone oils, which are attributed to the generation of the compressional wave in the droplets. The present work has shown some phenomena which need to be taken into consideration when using the droplet QCM as a rheological sensor and may stimulate the ongoing research on the related issues in the QCM community.

Key words: Quartz Crystal Microbalance, viscoelasticity, interfacial slippage, compressional wave

1. Introduction

The quartz crystal microbalance (QCM) is typically consisted of a thin disk of an AT-cut quartz crystal with circular metal electrodes on both surfaces. The QCM has been widely used to monitor the thickness change of film deposition according to the Sauerbrey equation [1] which relates the decrease in frequency Δf of the QCM and the added mass Δm of the thin film rigidly coupled to the crystal surface:

$$\Delta f = -\frac{2f_0^2}{A\sqrt{\rho_q\mu_q}}\Delta m \quad (1)$$

where f_0 is the crystal fundamental frequency, A is the piezoelectric active area, ρ_q and μ_q are the density (2650 kgm⁻³) and the shear modulus (2.94×10¹⁰ Nm⁻²) of the AT-cut quartz, respectively. When operating in liquid, the non-rigid mass will not oscillate in phase with the underlying crystal. An evanescent thickness-shear-mode (TSM) wave is generated near the interface region which is characterized by a decay length as:

$$\delta = \sqrt{\frac{\eta_L}{\pi f_0 \rho_L}} \quad (2)$$

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where ρ_L and η_L are the liquid viscosity and density, respectively. The decay length for water ($\rho_L = 10^3 \text{ kgm}^{-3}$ and $\eta_L = 10^{-3} \text{ Nm}^{-2}$) contacting a 5 MHz quartz crystal is about 250 nm. The change in frequency of the QCM with one surface fully covered by a Newtonian fluid is characterized by the Kanazawa equation [2]:

$$\Delta f = -f_0^{3/2} \sqrt{\frac{\rho_L \eta_L}{\pi \rho_q \mu_q}} \quad (3)$$

The Kanazawa equation is valid for a crystal of infinite lateral size which assumes a uniform shear velocity distribution across the crystal surface. However, a real crystal of finite lateral size results in a non-uniform distribution and hence a radial dependent of mass sensitivity that is greatest at the center and decreases toward the perimeter in an approximately Gaussian fashion [3, 4].

In terms of mass conservation, the compressional wave normal to the contact surface will generate in fluid due to the variation of the in-plane flow [3]. While the shear wave decays rapidly in a short distance at the fluid-crystal interface, the compressional wave can propagate a considerable distance in fluid and reflect back to the fluid-crystal interface to affect the crystal's response. Generation of the compressional wave has been confirmed by the interference experiments consisting of a fluid cavity confined between a QCM and a flat glass reflector [3, 5-7]. If the spacing of the fluid cavity reaches a multiple of $\lambda_c/2$ (λ_c is the compressional wave length), the constructive interferences of the acoustic wave will happen and the discontinuities in the frequency measurements of the QCM can be observed. The free surface of the fluid layer can also act as a reflecting surface of the compressional waves and perturb the crystal's oscillating response.

In biomedical and pharmaceutical industries, the fluid samples for rheological analysis are often expensive or available in small volume. It has stimulated the development of the droplet QCM loaded with a small droplet to perform certain analysis. Several studies reported the applications of the droplet QCM for assessing the viscosity of liquids [8-10]. It has also been used to investigate the dynamic wetting phenomena of liquids and the evaporation of droplets of volatile liquids [11-14]. In these studies, the generation of compressional wave was observed in the frequency measurements albeit few being discussed in detail. McKenna et al. [15] have studied the response of the QCM in contact with small water droplet by using simultaneous frequency measurements and video microscopy. The experimental results suggest that the compressional wave generation would happen when the droplet height reaches integer multiples of a half of the acoustic wavelength. Couturier et al. [16] have also reported the correlation between the size of the water droplet and the compressional wave generation in both the experimental measurements and the finite element simulations.

In this article, we first report the experimental results of the QCM responses due to the deposition of microliter droplets of silicone oils. The silicone oils with viscosity in a range from 50cS to 10³cS are tested. It has been found that the responses in the frequency and resistance measurements of the QCM in contact with the silicone oils are different from the Newtonian liquids. More importantly, it has been found that for the silicone oils the frequency of the QCM steadily increases for several hours and even exceeds the initial value of the unloaded QCM which has resulted in the positive frequency shift. Collaborative effects of interfacial slip and viscoelasticity have recently been discussed to qualitatively interpret the positive frequency shift. Secondly, we discuss the cyclical variations in the frequency and resistance measurements of the QCM during the silicone oil experiments, which are attributed to the generation of the compressional wave in the droplets. In the scenario of spreading hydrodynamics, the eigenmodes of the compressional wave in the droplets are also calculated by the finite element computation and compared with the experimental results.

2. Experiment

The experimental setup is shown in Figure 1. The 5 MHz AT-cut quartz crystals (diameter of 25.4 mm and thickness of 0.33 mm) were used. Polished gold electrodes (~ 160 nm) were deposited on chromium adhesion layers (~ 15 nm) on both sides. An asymmetric pattern was adopted, where the upper electrode in contact with the fluid media had a larger radius ($r_e^{\text{upper}} = 6.45 \text{ mm}$) than the lower one ($r_e^{\text{lower}} = 3.3 \text{ mm}$). The crystal sensor was driven by a Research Quartz Crystal Microbalance (RQCM) (Maxtek Inc.). A PC was linked to the RQCM to record the changes in the resonant frequency and dissipation of the crystal. The crystal holder was enclosed in a chamber, where the temperature and relative humidity were controlled as $23 \pm 0.5^\circ \text{C}$ and $60 \pm 5\%$.

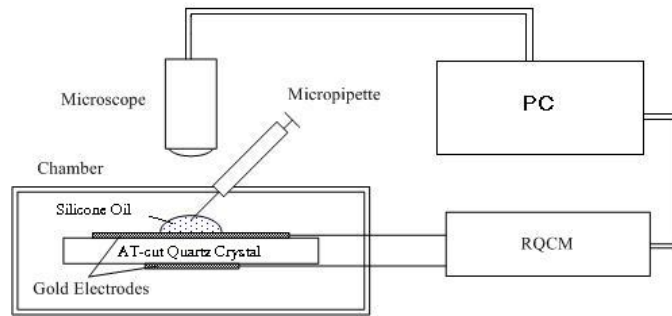
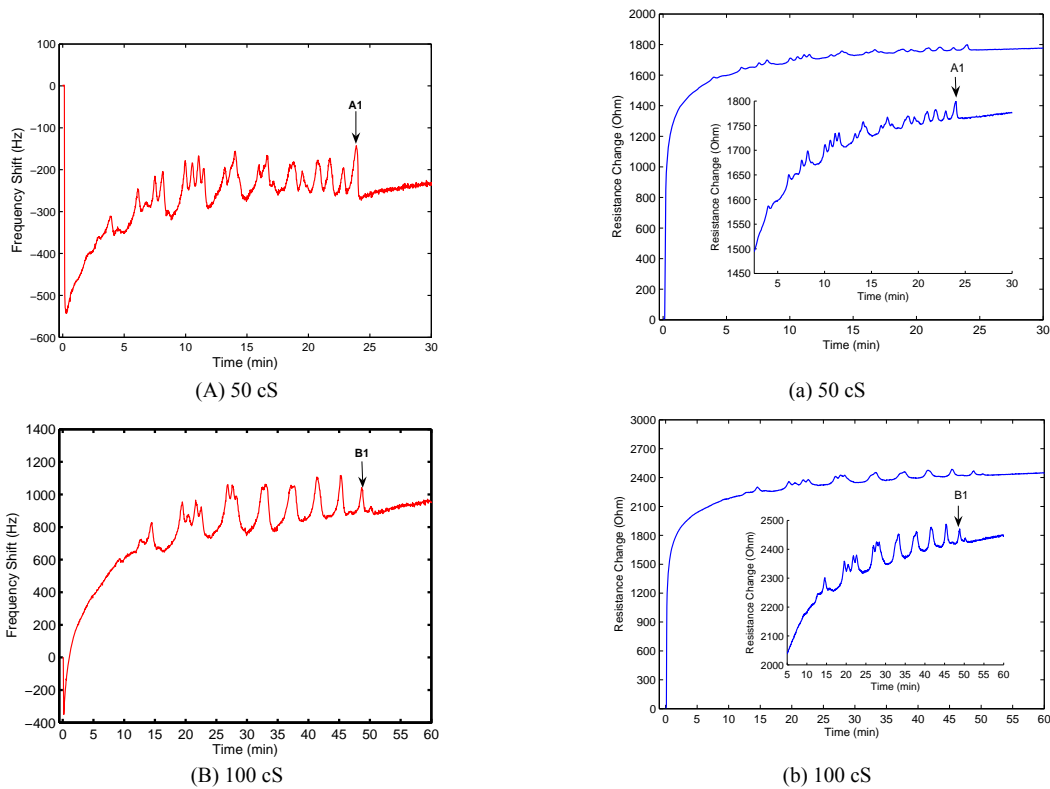


Figure 1 Schematic diagram of the experimental setup.

Droplets of KF96 silicone oils (Shin-Estu Chemical) with the viscosity ranging from 50 cS to 10^3 cS were deposited to the top electrode of the crystal by a digital pipet. The volume was 2 μ L. Microscopy with crosshair reticule was focused to center the droplet. The measurements for silicone oils would be for at least 6 h for the crystal's responses to be stabilized and exhibit the long term trend. Crystals after use were washed thoroughly in xylene (Fisher Scientific) and dried in air until the initial values of the frequency and resistance under the unloaded condition were obtained.

3. Results and Discussion



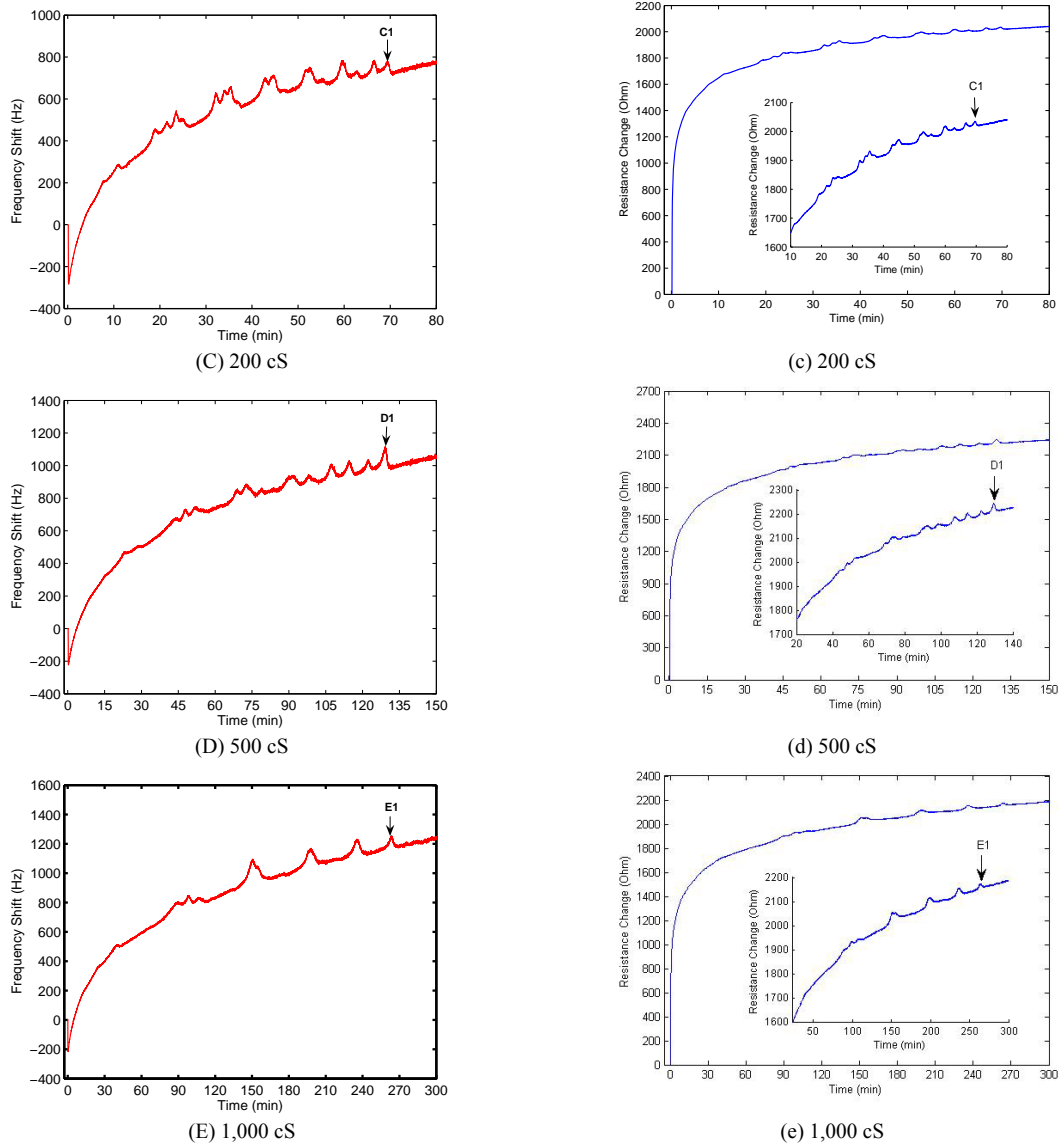


Figure 2 Changes in resonant frequency (A-E) and resistance (a-e) with time for silicone oils with different viscosities. The detailed views on a smaller scale are inserted in (a-e). The peaks, marked as A1~E1, correspond to the compressional wave resonances when the central heights of the droplets reach $\lambda c/2$.

Figure 2 shows the real-time changes in the resonant frequency and resistance of the crystal in contact with silicone oils with viscosity in the range of $50\sim 10^3$ cS. The initial frequency decrease and resistance increase in the first few minutes ($\Delta f = -200 \sim -550$ Hz and $\Delta R = 1000\sim 1200$ Ω) were due to the coverage of the droplet on the electrode of the crystal. Thereafter, the response of the crystal sensor upon the silicone oil droplet exhibited a complicated long term trend, where the frequency and resistance increased steadily with time. The magnitudes and kinetics of the increments were dependent on viscosity of the silicone oils. It has been studied by our group that the positive changes in the frequency and resistance of the crystal could be explained by the combined effects of the fluid viscoelasticity and interfacial slippage [17]. If we denote the frequency shift given by Eq.(3) as Δf_K , we can obtain a modified equation which accounts for effects of the fluid viscoelasticity and interfacial slippage:

$$\Delta f = \chi_f \Delta f_K \quad (4)$$

where

$$\chi_f = \text{Re} \left[\left(1 - \frac{2b}{\delta} - i \right) \left(1 - i \frac{\eta''}{\eta'} \right)^{1/2} \right] \quad (5)$$

χ_f denotes the correction factor of the frequency shift. Parameters b/δ and η'/η'' represent the contributions on the frequency shift of the QCM from the fluid viscoelasticity and interfacial slippage, respectively. As shown in Figure 3, when b/δ or η'/η'' changes, the frequency shift of QCM calculated by Eqs.(4) and (5) will be different from Δf_K which is caused by a Newtonian liquid loading. More importantly, it is found in Figure 3 that the extreme combination of b/δ or η'/η'' could give rise to the change in sign of χ_f (or Δf), which means that the resonant frequency can be even higher than the unloaded QCM.

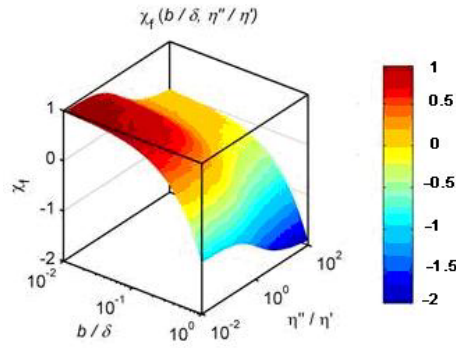


Figure 3 Calculated correction factor of the frequency shift χ_f versus the ratio of the slip length to the decay length b/δ and the inverse loss factor η''/η' .

As shown in Figure 2, there are periodical peaks in the frequency relative to the upshift background. It has also found the similar peaks in the motional resistance plots. Typically the droplet height for 10^3 cS oil sample is ca.1mm whereas the decay length of the shear wave at 5MHz is ca.8 μ m. Given that the droplet height is easily in excess of the decay length, the shear wave is not responsible for the resonant peaks in frequency. Hence, it is assumed that the resonant peaks in frequency are caused by the decrease in the compliance of the crystal due to the generation of the compressional wave. And the compressional wave radiation would contribute to the energy loss which resulted in the additional resistance. The silicone oil droplet herein acts as an acoustic cavity for the compressional wave which could propagate to the free surface of the droplet and reflect. The constructive interference happens if the droplet height is equal to multiple $\lambda c/2$ (λc is the compressional wavelength). To verify our assumption, it requires to determinate the droplet heights in real time. However, the droplet edges taken in the microscopy images were found to be vague due to light scattering, though it may be improved by using a higher-resolution camera. Alternatively, we have adopted a hydrodynamic model to simulate the evolution of the central height and the contact radii of the spreading droplet [13, 18]. It assumes that a small droplet can be approximated as a spherical cap and that its central height h_c is much smaller than its base radius r_b if its contact angle $\theta \ll 90^\circ$. Without going to the details, we can derive two key equations of the time dependency of r_b and h_c :

$$r_b^{3m+1} = \frac{\gamma_{LV}}{\eta_L} t V^m \quad (6)$$

$$h_c = \frac{2}{\pi} \left(\frac{\gamma_{LV}}{\eta_L} t \right)^{\frac{-2}{3m+1}} V^{\frac{m+1}{3m+1}} \quad (7)$$

where γ_{LV} the surface tension of the liquid and m for silicone oils is 3.6 and slightly affected by the viscosity.

The smallest droplet height which favors compressional wave resonance should in principle be equal to $\lambda c/2$, which in our experiments correspond to the last resonant peaks, noted as A1, B1, C1, D1 and E1 in Figure 2. The peaks (A1~E1) were measured at time $t^{\text{exp}} = 23.9, 48.7, 69.5, 129.3$ and 263.8 min depending on the viscosity of the silicone oils. Using Eqs.(6) and (7), we can calculate the changes in the central height h_c versus time for varying viscosity, shown in Figure 4. Then the instances in time for the resonant peaks (A1~E1) at heights of $\lambda c/2$ can be estimated by intersections of the curves and the horizontal line at $h_c = \lambda c/2$ ($\lambda c \sim 0.2$ mm in silicone oil at 5MHz). The calculated instances in time $t^{\text{cal}} = 23.8, 47.7, 69.7, 127.0$ and 262.1 min show good agreement with the experimental ones t^{exp} .

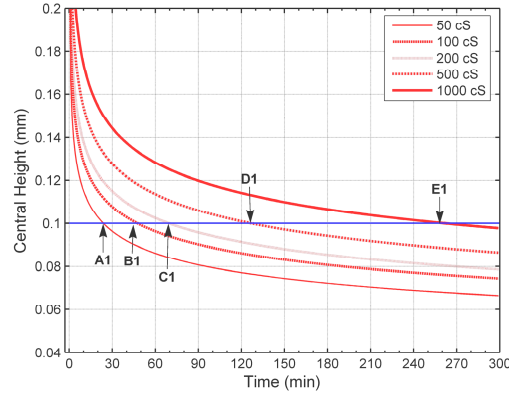


Figure 4 Changes in the central height of the droplets with time for silicone oils with different viscosities. The resonant peaks, noted as A1~E1, correspond to the compressional wave resonances when the central heights of the droplets reach $\lambda_c / 2$.

We have also used the finite element computation to ascertain if the resonant peaks in frequency during the spreading processes appear at the well-defined droplet heights which are equal to integral multiples of $\lambda c/2$. The droplet heights can be determined by the hydrodynamic model, whereas the values of the acoustic wavelengths against the varying shapes of the droplets are unknown. Herein we have followed the approach by Couturier et al. [16] to calculate the eigenmodes of a spherical cap consisting of perfect fluid without viscosity. To the first order, the shear waves are uncoupled with the compressional waves across most of the droplets, which is important for our finite element computation to resolve the compressional wave contribution. We built a 3D geometry model of spherical cap of radius R_s where r_b and h_c denote the base radius and central height, respectively. The time instances to exhibit the resonant peaks (a-i) in Figure 5 can be obtained from the frequency plot. The corresponding base radius and central height can be calculated by using Eqs. (6) and (7) when the material properties and volume of the droplet are known. The plot of the central heights versus the base radii for 10^3 cS silicone oil is given in Figure 5. The relation $R_s = (r_b^2 + h_c^2) / 2h_c$ is used to calculate the values of R_s . For the finite element computation, the boundary conditions are that acoustic pressure $p=0$ at the air-fluid interface and zero velocity ($n\nabla p = 0$) at the solid-fluid interface.

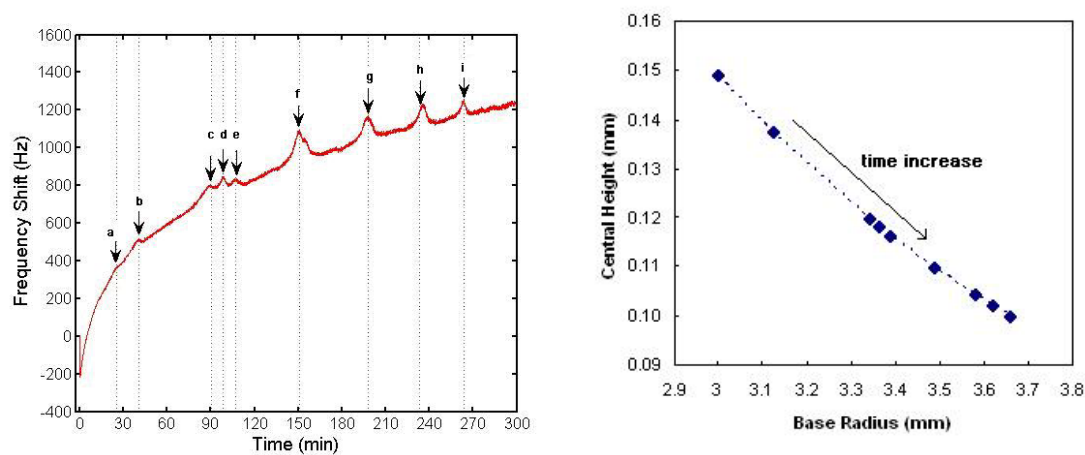


Figure 5 Left: The measured frequency shift with time for 10^3 cS silicone oil. Arrows (a~i) mark the time instances of the frequency peaks. Right: Central height of the droplet versus the base radius calculated by Eqs.(6)(7), associating with the increasing time.

Based on the above 3D model and boundary conditions, we apply the commercial finite element software ABAQUS (www.simulia.com) to calculate the eigenmodes and the eigenfrequencies in a spherical cap. For 10^3 cS silicone oil, Table 1 summarizes the simulation results, giving the eigenfrequencies at compressional mode for varying droplet shapes. As the sound speed in 10^3 cS silicone oil is 987.3 m/s, the corresponding wavelengths λ_c can be calculated. It is found that when the shape of the droplet changes during the spreading process, the compressional mode eigenfrequency f^{com} increases with the base radius whereas the corresponding wavelength λ_c decreases. However, it is worth noticing that the ratio of h_c to λ_c is approximately unchanged at 0.49 ($\pm 2\%$). It supports the idea that the resonant peaks in the frequency and resistance appear at the well-defined droplet heights. The droplets acting as resonant cavities for compressional wave generation are favor to exhibit resonance behavior at time instances where the droplet heights at the center of the wetted area $h_c = \lambda_c/2$.

Table 1 Simulation results of the eigenfrequency and wavelength at compressional mode for 10^3 cS silicone oil droplet.

No.	Time t (sec)	Base Radius rb (mm)	Central Height hc (mm)	Eigenfrequency f^{com} (MHz)	Wavelength λ_c (mm)	Ratio h_c / λ_c
1	1507	2.999	0.149	3.58171	0.2756	0.5395
2	2423	3.122	0.137	3.64017	0.2711	0.5060
3	5425	3.342	0.120	4.01625	0.2458	0.4871
4	5908	3.366	0.118	4.05288	0.2435	0.4845
5	6430	3.390	0.116	4.10409	0.2405	0.4837
6	9047	3.489	0.110	4.31477	0.2287	0.4800
7	11892	3.581	0.104	4.56126	0.2164	0.4819
8	13982	3.620	0.102	4.59025	0.2150	0.4744
9	15809	3.658	0.100	4.70737	0.2097	0.4765

4. Conclusion

Droplet quartz crystal microbalance has been demonstrated to be a promising tool for accessing rheological properties of liquid samples used in biomedical and pharmaceutical industries. However, the QCM must be used with caution because several factors such as liquid viscosity/viscoelasticity and interfacial slippage can affect the measurement readings in a collaborative way. In addition, when a microliter droplet is placed on the surface of the crystal with finite lateral size, the mass sensitivity of the crystal is not uniform across the surface, which can result in the surface normal flow and generate the compressional waves. In this article, we have first reported the experimental results of the QCM responses due to the

deposition of microliter droplets of silicone oils with viscosity ranging from 50cS to 10^3 cS. It has found that the QCM responses in contact with the silicone oils are different from the Newtonian liquids. More importantly, it has been found that for the silicone oils the frequency of the QCM steadily increases for several hours and even exceeds the initial value of the unloaded QCM which has resulted in the positive frequency changes. The collaborative effects of the interfacial slip and viscoelasticity have been discussed to qualitatively interpret the positive frequency changes. Secondly, we have discussed in detail the cyclical variations in the frequency and resistance measurements of the QCM, which could be caused by the generation of the compressional waves in the droplets. The experimental results have been compared with the theoretical ones predicted by the finite element computation associated with a hydrodynamic model. Good agreement between theory and experiment has been obtained. The finding supports to the idea that the small droplets on the crystal could act as resonant cavities for the generation of compressional waves and that the greatest propensity to exhibit periodical resonant behavior is at droplet height of $\lambda c/2$ above the crystal-oil interface. The present work has highlighted some phenomena worth to be taken into consideration when using the droplet QCM as a rheological sensor and may stimulate the ongoing research on the related issues in the QCM community.

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