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Response of Quartz Crystal Microbalance Loaded with Single-drop Liquid in Gas Phase

Li Yang[1,2,*] and Xianhe Huang[1]

[1]*Frequency Control Laboratory, School of Automation & Engineering, University of Electronic Science and Technology of China, Chengdu, 610054, China*

[2]*College of Electrical & Information Engineering, Southwest University for Nationalities , Chengdu, 610041,China*

Abstract: The frequency response of quartz crystal microbalance loaded by single-drop liquid is studied in this paper. Previous studies have shown that the relationship between resonant frequency and properties of liquid by completely immersing one side of the crystal in liquid. In this work, only localized portion of crystal was wetted by liquid droplet. Repeated experiment shows the relationship between liquid property include viscosity and density to resonant frequency. Furthermore, Theoretical formula describing the frequency change of the quartz crystal microbalance with liquid property is proposed. The predicted results showed distinct coincide with experimental results.

Keywords: Quartz crystal microbalance, single-drop, gas phase.

1. INTRODUCTION

The quartz crystal microbalance(QCM) has been widely used as highly sensitive sensor which commonly configure with electrode on both sides of a thin disk AT-cut quartz. The crystal can be electrically excited into resonance because of the piezoelectric properties. In the late 1950s, Sauerbrey found the relationship between resonant frequency and mass deposit on surface of quartz in gas phase [1],

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

Where Δf is the observed frequency change (in Hz), μ_q is the shear modulus, ρ_q is the density of the crystal, A is the active electrode area ,and Δm is the mass change on the surface of the crystal (in ng). For the AT-cut quartz crystal (ρ_q =2.65 g/cm^3, μ_q=2.95N/m^2). Since the work of Sauerbrey, the QCM has been widely used to monitor slight mass change(nanogram) in many research areas include biology, physics, medicine and so on. In the late 1980s, Kanazawa found the QCM oscillate in contact with liquid, the relationship between liquid property (such as viscosity, density) and resonant frequency was founded while immerse one surface of crystal in liquid [2]. The equation showed as follow:

$$\Delta f = -f_0\left(\frac{\rho\eta}{\pi\mu_q\,\rho_q}\right)^{\frac{1}{2}} \tag{2}$$

Where Δf is the difference in resonant frequency between the coated and bare crystal, η is the viscosity of liquid and ρ is the density of the liquid.it therefore extend the application of QCM to liquid media.

For Sauerbrey equation, the deposit thin film should be rigid thin and for Kanazawa equation, one surface of crystal should be immersed in liquid. if a microliter liquid dropped on the surface of QCM, the Sauerbrey equation and Kanazawa equation may not suitable for the interpretation of the frequency response of QCM. However, if the frequency response of QCM loaded by liquid droplet could be figured out, the condition that immerse one surface of crystal in liquid could be changed to drop one microliter liquid on surface of crystal, then, the application of QCM would be extended to more area and it must be more convenient.

In this paper, the frequency response of QCM loaded by liquid droplet was investigated. In particular, the resonant frequency shift was discussed in relation to the property of liquid such as viscosity and density. In addition, the resonant frequency of QCM loaded by microliter liquid has been measured. The results predicted by the theoretical model and obtained by the experiments are compared.

2. PRINCIPLES OF QCM LOADED BY LIQUID DROP

Liquid droplet resting on the surface of crystal takes the shape of a spherical cap, like (Fig. **1**).

In which, r_d is the base radius for liquid droplet, r_e is the electrode radius; the r_d smaller than r_e. Because it has small volume, the distort by gravity may negligent. Owing to the Newtonian properties of the liquid, the Liquid films in contact with the QCM do not behave as rigid layers and the films does not oscillate as a whole in sympathy with the crystal. With the drop of liquid, the frequency of the AT-cut crystal resonator would decreased and the frequency change can be described as follow [3]:

$$\Delta \mathrm{f} = \frac{1}{\pi r_d^2}\int_0^{2\pi}\int_0^{r_d} S(r,\theta)m\,(r,\theta)rdrd\theta \tag{3}$$

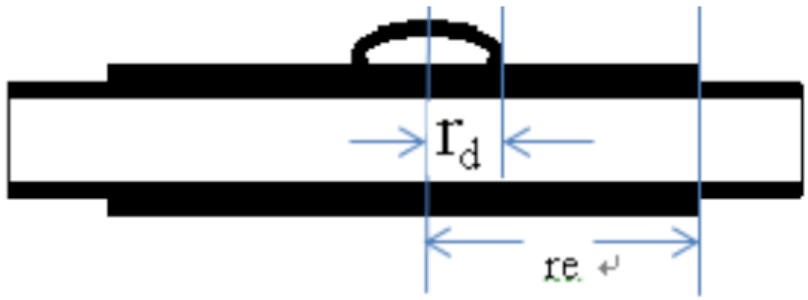

Fig. (1). Schematic view of single-drop liquid localized on the QCM surface.

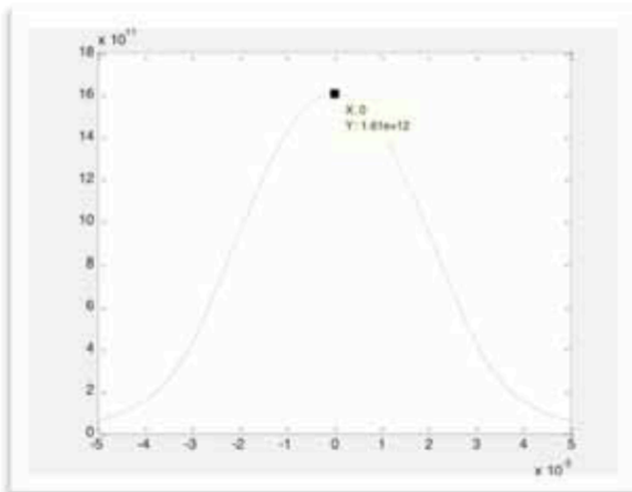

Fig. (2). The mass sensitivity along the radial direction.

In which, S(r, θ) is mass sensitivity function and represents the differential frequency change per mass change at a specific location, Δm(r, θ) is the effective added mass, r_d is the radius for the localized or nonuniform mass deposit on the electrode, r and θ are the polar coordinates of the point at which the mass is added. Mass sensitivity function could be calculated by equation (4):

$$\mathrm{S(r)} = \frac{|u_1(r)|^2}{2\pi\int_0^\infty |u_1(r)|^2 r dr} C_f \tag{4}$$

Where $u_1(r)$ is particle displacement amplitude ,C_f is sauerbery's sensitivity constant, r is the distant from center. For particle displacement amplitude, the function could be written as equation [4] (5).

$$u_1(x_1, x_2, x_3, t) = u_1(x_1, x_3)\sin(k_2\, x_2)\cos\omega t \tag{5}$$

The surface plane of gold electrode was defined by (x_1,x_3), k_2 is the shear horizontal acoustic wavenumber in the X_2 direction. The equation (5) could be reduced as:

$$\frac{c_{11}}{c_{66}}\frac{\partial^2 u_1(r)}{\partial x_1^2} + \frac{c_{55}}{c_{66}}\frac{\partial^2 u_1}{\partial x_3^2} + \frac{\omega^2-\omega_i^2}{c^2}u_1(r) = 0 \tag{6}$$

Where C_{ij} represent the elastic stiffness constant; $\omega_i = k_2\sqrt{\frac{c_{66}}{\rho}}$ is cutoff frequency, $c = \sqrt{\frac{c_{66}}{\rho}}$ is the acoustic wave velocity in crystal. Convert equation (6) into polar coordinate:

$$r^2\frac{\partial^2 u_1(r)}{\partial r^2} + \frac{\partial u_1(r)}{\partial r} + \frac{K_I^2 r^2}{A}u_1(r) = 0 \tag{7}$$

The equation (7) is a Bessel differential equation and the general solution could be shown as

$$u_1(r) = \begin{matrix} C_1 J_0\left(\frac{K_I}{\sqrt{A}}r\right) + C_2 N_0\left(\frac{K_I}{\sqrt{A}}r\right) \\ C_1 I_0\left(\frac{K_I}{\sqrt{A}}r\right) + C_2 K_0\left(\frac{K_I}{\sqrt{A}}r\right) \end{matrix} \tag{8}$$

Where J_0, Y_0, I_0, and K_0 are the Bessel's functions of the first and second kind with order zero and the modified Bessel's function of the first and second kind with order zero. The particle displacement amplitude $u_1(r)$ could be calculated by function (8), submitted solution into equation (4), the mass sensitivity functions(r) could be calculated. In this study, a 3rd overtone 10 MHz AT-cut crystal was used. The electrode radius and thickness are set as 1000$\dot{A}$ and 3mm respectively. Fig. (**2**) shows the variations of the differential mass sensitivity along the radial direction.

From Fig. (**2**) we can see that the mass sensitivity of the QCM is the largest in the center of electrode and decrease monotonically along the radial direct. Notably, the mass

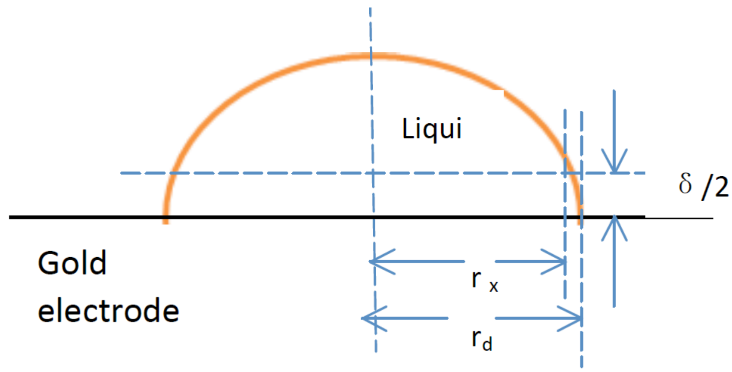

Fig. (3). View of single-drop liquid droplet on the gold electrode.

sensitivity of the QCM can be described as Gaussian function, like equation (9):

$$S(r) = Ke^{-\beta\frac{r^2}{r_e^2}} \tag{9}$$

Where $K = 1.6{\times}10^{12} Hz/Kg$ is the largest sensitivity for QCM at the center of electrode, re is the radius of the gold electrode and ß is the constant.

In this study, the volume of sing-drop liquid was 0.5 μ l and The view of 0.5 µ l liquid droplet on the gold electrode surface was shown by Fig. (**3**).

In which, $\frac{\delta}{2} = \frac{1}{2}\sqrt{\frac{\eta}{\pi f_0 \rho}}$is the liquid decay length, and η is viscosity for liquid, ρ is the density for liquid,$f_0$is fundamental resonant frequency for QCM. r_x is the base radius for liquid droplet contain with decay length, rd is the base radius between liquid droplet to gold electrode.

The resonant frequency was shifted after liquid dropped on the surface of gold electrode, and it can be calculated as equation (10):

$$\Delta f = \frac{2\pi}{\pi r_x^2}\int_0^{r_x} ke^{-\beta\frac{r^2}{r_e^2}}\Delta m_1\, rdr + \frac{1}{\pi(r_d - r_x)^2}\int_{r_x}^{r_d} ke^{-\beta\frac{r^2}{r_e^2}}\Delta m_2\, rdr \tag{10}$$

In which,$\Delta m_1 = \rho\pi r_x^2 \frac{\delta}{2}$ is the effective mass of the liquid droplet contain within decay length $\frac{\delta}{2}$ for base radius from center to r_x; Δm_2 is the effective mass of the liquid droplet contain within decay length for base radius from r_x to r_d. In this study, the decay length for water (25°C) equal to $0.84{\times}10^{-4}mm$, liquid thickness is large compared to the decay length , then, the Δm_2 is much smaller than Δm_1,the influence of the Δm_2 could be negligent, equation(10) could be reduced as follow:

$$\Delta f = \pi\delta\int_0^{r_x} ke^{-\beta\frac{r^2}{r_e^2}}\rho\, rdr \tag{11}$$

Then:

$$\Delta f = -\frac{1}{2}\pi\delta k\frac{r_e^2}{\beta}\rho[1 - e^{-\beta\frac{r_x^2}{r_e^2}}] \tag{12}$$

Consider$r_x \ll r_e$, equation (12) could be simplified to equation 13:

$$\Delta f = -\frac{1}{2}\pi\delta k r_x^2\rho \tag{13}$$

According to equation (13), the resonant frequency shift of QCM loaded by liquid droplet could be calculated.

3. EXPERIMENTAL SECTION

3.1. Materials and Apparatus

All the PZ crystals were AT-cut with a resonance frequency of 10 MHz. The crystal **(**diameter: 8 mm, thickness: 0.185 mm) was placed between two gold electrodes, mounted in metal holder with a plug. An symmetric electrode pattern was used so that the upper electrode and the lower electrode had same radius (3 mm). They were purchased from Tangshan JingYuan YuFeng Electronics co., Ltd (Hebei, China). The quartz crystal was driven at its resonant frequency with a homemade oscillator circuit and frequency measurement was performed with Agilent 531323a, with a precision of 0.1 Hz at a gate time of 0.1 s. Micro-injector (range from 0.2ul to 10ul) was obtained from KeXiao co., Ltd (Hang Zhou, China).

Phosphate-buffered saline (PBS) was composed of 137 mM NaOH, 2.7 mM KCL, 8.0 mM Na_2HPO_4, and 1.5 mM KH_2PO_4 (pH 7.2).

3.2. Measurements

In order to guarantee that possible contaminants were removed, the QCM was dipped in 1.0 M NaOH for 10 min and in 1.0 M HCL for 10 min and then washed with distilled water at room temperature. After cleaning procedure, the crystal was air drying and the basic frequency (F_0) was taken. Then, the liquid dropped on the center of electrode surface using Micro-injector. In order to got the more information about the frequency response for liquid droplet, three different solutions include water, 0.01g/ml Nacl, 0.1 g/ml Nacl were choose in this study. The different solution had different viscosity and different. All the experiments used same method and were conducted at same condition, include same temperature (25°C), same humidity (60) and same crystal

Table 1. Result of frequency shift with same liquid volume (0.5µl).

Crystal Number	Δf(Hz) (0.5µl)		
	water	0.01g/mlNaCl	0.1g/mlNaCl
1	121	213	238
2	132	184	225
3	112	238	230
4	138	167	221
5	105	177	220
6	108	176	223
average	119	192	226

Table 2. Comparison between measured data to calculated data.

Liquid (0.5µl)	Measured Data (average)	Calculated Data
Water	119Hz	125Hz
0.01g/mlNaCl	192 Hz	198Hz
0.1g/mlNaCl	226 Hz	230Hz

contours. Because of the symmetric electrode pattern, the device had high uniform mass sensitivity distribution [5-7].

4. DATA AND ANALYSIS

4.1. Effect of the Viscosity

Three different liquids include distill water, 0.01g/ml NaCl and 0.1g/ml NaCl were used in this study. The volume of liquid used in this experimental were o.5 μ l and All the liquid dropped on the center of the gold electrode. After liquid dropped, the resonant frequency (F_1) measured by frequency counter (Agilent 531323a).

the resonant frequency shift were calculated by equation(14)

$$\Delta f = F_1 - F_0 \tag{14}$$

The experiments were repeated 6 times and the experimental results are summarized in (Table **1**),

It is obviously to see from (Table **1**) that the resonant frequency of all crystals decreased after liquid dropped on the center of gold electrode. It therefore founded that both the Sauerbrey and the Kanazawa equations may not be suitable for the interpretation of the frequency response of the QCM loaded by liquid droplet. The average frequency shift induced by 0.5 μ l water was 119Hz, induced by 0.01g/mlNaCl was 192Hz and induced by 0.1g/mlNaCl was 205Hz. the experimental data indicated that the greater of the viscosity, the greater of the resonant frequency shift. In this study, the viscosity for water (25) was0.8937$mpa \cdot s$,and the viscosity for 0.1g/mlNaCl (25) was1.039 $mpa \cdot s$,after drop the same volume on the gold electrode surface,the frequency shift induced by Nacl higher than water. Increased viscosity apparently increased the frequency shift. The resonant frequency shifted on account of the effective mass of liquid droplet contained within this decay length. The decay length (δ) depend on the viscosity (η). If the viscosity and density of solution were increased, the decay length was increased, afterwards the resonant frequency decreased.

4.2. Comparison Between Measured Data to Calculated Data

In this study, three different liquid that had different viscosity and density were used for experimental. The resonant frequency shifted for different liquid could be calculated by equation (13). (Table **2**) shows the frequency shift of the QCM as a liquid was dropped on the center of the gold electrode.

it is obviously to see from table3, all measured data had slight difference to calculated data. It can be deduced from above results: first, Sauerbrey and the Kanazawa equations may not suitable for liquid droplet on surface of QCM. Second, the viscosity and density would influence the resonant frequency. Third, the calculated data get from equation (13) agrees fairly will with the measured data.

CONCLUSION

The frequency response of QCM loaded by different liquid droplet was discussed in this study. Experiment data shows the relationship between liquid property include viscosity and density to resonant frequency, and the calculated data get from Theoretical formula which deduced in this paper agrees fairly will with the measured data.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

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