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MINI-REVIEW

From Quartz Crystal Microbalance to Fundamental Principles of Mass Measurements

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Abstract: This article reveals that the mass sensitivity of the quartz crystal microbalance (QCM) is acceleration dependent and this feature is not specific to only the QCM, but also is valid in the case of other balances. During quartz crystal vibration a megagravity field is created at the surface of the quartz resonator. The existence of this field is demonstrated using C-nanoparticles deposition. It is shown that the product of the minimum detectable mass and the acceleration acting on that mass is a constant for both QCM and beam balances, thus, explaining why QCM is more sensitive than are conventional analytical microbalances. The article introduces the concept of acceleration-dependent mass sensitivity and explains the origins of QCM sensitivity to a liquid viscosity. Based on this concept, several fundamental principles for mass measurements are formulated.

Keywords: Acceleration, beam balance, QCM, megagravity field, equivalence principle, general relativity

INTRODUCTION

Measuring lengths and masses were probably the earliest challenges of mankind.

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When King Hiero of Syracuse asked Archimedes (285–212 BC) whether his new crown was really made of pure gold, the philosopher immersed the crown and an equal weight of pure gold, attached to the arms of a beam balance, into a vessel of water where the crown seemed to be lighter. According to Archimedes' principle, the pan of the beam balance on which the crown was laid was pushed upwards because the crown displaced a volume of water larger than that displaced by the pure gold laid on the other pan of the balance. This was a clear evidence of the fact that the goldsmith had intermixed some lighter metal, probably silver. The additional volume of water displaced by the crown could weight several 10s of grams, which were easily detected at that time.

The balances we use today in our laboratories, e.g., beam, cantilever, torsion, or spring balances, depending on their maximal load, can detect even 10^{-10} kg.

On the other hand, the quartz crystal microbalance (QCM), which became a largely used instrument during the last decades, can detect up to 10^{-16} kg.

Since the quartz crystal microbalance was first introduced by Sauerbrey in 1959, it has become a largely used instrument for small mass measurements in vacuum, gas, and liquid phase (Ballantine et al. 1997; Lu and Czanderna 1984; Martin et al. 1991; Kanazawa and Gordon 1985; Martin et al. 1993; O'Sullivan and Guilbault 1999; Rodahl and Kasemo 1996; Marx 2003; Mecea 1994). Several questions related to QCM work are still lacking a sound explanation:

- Why is QCM more sensitive than conventional analytical microbalances?
- Why must the deposition on the surface of a quartz resonator be adherent to its surface?
- Why does the frequency response of the QCM in contact with a liquid depend on the liquid viscosity and quartz resonator surface roughness?

The aim of the article is to provide an answer to these questions and to put some light on the more general problem of mass measurement.

SENSITIVITY ANALYSIS

Quartz Crystal Microbalance

Ever since the use of quartz crystal resonators for frequency control applications in radio-communication equipment began, the effect of a foreign material deposited on their surfaces on their resonant frequency has been known. However, a quantitative relationship was not established until 1959. The possibility of using quartz crystal resonators as quantitative mass

measuring devices was first explored by (Sauerbrey 1959). The decrease of the resonant frequency of a thickness shear vibrating quartz crystal resonator, having AT or BT cut, was found to be proportional to the added mass of the deposited film:

$$\Delta f = -\frac{f_q^2 M_f}{N\rho_q S} = -\frac{f_q^2 m_f}{N\rho_q} \tag{1}$$

where f_q is the fundamental resonant frequency of the quartz, N is the frequency constant of the specific crystal cut ($N_{AT} = 1.67 \times 10^5\,\mathrm{Hz \cdot cm}$; $N_{BT} = 2.5 \times 10^5\,\mathrm{Hz \cdot cm}$), $\rho_q = 2.65\,\mathrm{kg/dm^3}$ is the quartz density, and S is the surface area of the deposited film, the mass of which is M_f. When the deposited film covers the whole sensitive area of the quartz resonator it is easier to use the areal density, $m_f = M_f/S$, to further calculate the film thickness, $l_f = m_f/\rho_f$, where ρ_f is the density of the deposited film. A typical quartz crystal resonator is shown in Fig. 1.

The keyhole-shaped electrodes on both major faces of the quartz resonator are vacuum deposited gold or silver films, about 150 nm in thickness. The mass-sensitive area is situated in the central part of the resonator, covering about the area where the two electrodes overlap.

Equation (1) shows that the QCM mass sensitivity, $\Delta f/m_f$, is proportional to the square of the quartz resonator frequency.

There are also experimental data showing that on the surface of a quartz crystal resonator we have a mass sensitivity distribution that closely follows the vibration amplitude distribution. In Fig. 2 experimental results published elsewhere are shown (Mecea 1994, 1989). The recorded frequency change for deposited silver spots, which have the same mass, M_f, is proportional to the vibration amplitude in that point indicated by the voltage, U. A 5 MHz, plano-convex, AT-cut resonator with 200 mm curvature radius was used. The diameter of the resonator was 14 mm. It had silver electrodes of different diameters on each side: 13 mm on the flat side and 6 mm on the convex side. To reveal the mass sensitivity distribution, small silver spots having the same thickness and a diameter of 0.6 mm were vacuum

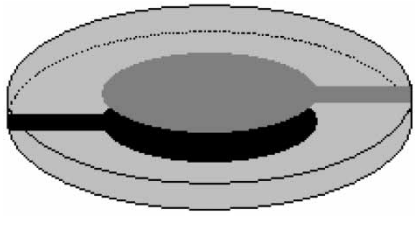

Figure 1. A typical quartz crystal resonator used for mass measurements.

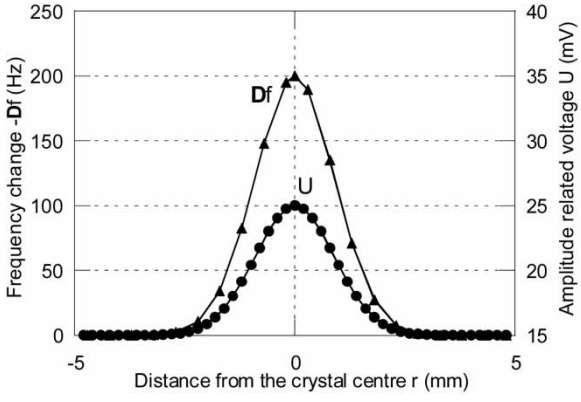

Figure 2. Mass sensitivity related Δf and vibration amplitude related U distribution along one of the quartz resonator diameters.

deposited along one of the crystal diameters, with 0.5 mm spacing between them. The amplitude distribution along the same diameter was revealed by using the scanning probe method (Mecea 1994, 1989). The voltage, U, is proportional to the vibration amplitude in each point along the chosen diameter. Similar results were reported in the literature (Sauerbrey 1959; Sauerbrey 1964; Mueller and White 1968; Martin and Hager 1989; Schneider and Martin 1995; Buttry and Ward 1992; Lucklum and Hauptman 1997).

Both the mass sensitivity and amplitude distribution curves follow a Gaussian function (Martin and Hager 1989). The displacement of a point, vibrating with simple harmonic motion, may be described as

$$x = A \sin(\omega t) \tag{2}$$

where A is the vibrational amplitude in that point and $\omega = 2\pi f$ is the angular frequency.

The acceleration of this motion is

$$a = -\omega^2 A \sin(\omega t) = -4\pi^2 f^2 A \sin(\omega t) \tag{3}$$

The maximum value of the acceleration in that point is $a_{max} = \omega^2 A$. On the crystal surface the highest vibration amplitude, A_0, and the maximum acceleration, $a_0 = \omega^2 A_0$, are in the center of the quartz resonator.

From Eq. (1) we conclude that the mass measuring sensitivity is proportional to the square of the quartz resonator frequency. From the experimental results shown in Fig. 2 we conclude that the mass measuring sensitivity of the QCM is proportional to the vibrating amplitude at that point. These two statements lead to the conclusion that the physical quantity that determines the mass measuring sensitivity in every point on

the surface of a quartz crystal resonator is the acceleration of the crystal vibration in that point.

Earlier experimental results in gas and vacuum (Sauerbrey 1964; Kanazawa 1997; Borowsky et al. 2000) indicated that the vibration amplitude in the center of a quartz resonator is in the range from 10 nm to 200 nm.

In order to correlate the mass measuring sensitivity in the center of the quartz crystal resonator with the corresponding acceleration in this point we shall rely on the previous results obtained for amplitude measurements in the center of a 5 MHz plano-plano AT-cut quartz resonator using scanning tunneling microscopy (Borowsky et al. 2000). Here it is stated that the maximum vibration amplitude in the center of such a crystal is

$$A_0 = CQV_d, \tag{4}$$

where $C = 1.4 \times 10^{-12}\,m/V$, Q is the quality factor of the quartz resonator, and V_d is the peak voltage applied on the quartz resonator electrodes.

A small silver spot with a diameter of 0.45 mm and thickness of 200 nm, measured with an adjacent film thickness monitor having a mass $M_f = 3.3399 \times 10^{-10}\,kg$ was vacuum deposited in the center of a 4951605 Hz plano-plano AT-cut quartz resonator. The frequency change, $\Delta f = 96.925\,Hz$, the crystal inductance, $L = 73\,mH$, and resistance, $R = 15\,\Omega$, were measured with a Hewlet Packard network analyzer model E 5100A, driving the crystal at $P = 100\,\mu W$. Calculating $Q = \omega L/R = 151411$ and $V_d = \sqrt{2PR} = 0.0548\,V$ we get $A_0 = 116.1\,Å$. The maximum acceleration is $a_0 = 1.1238 \times 10^7\,m/s^2 = 1.1456 \times 10^6\,g$, where $g = 9.81$ and m/s^2 is the gravitational acceleration. It shows that, in the center of a quartz crystal resonator, acceleration is more than one million times higher than is the gravitational acceleration. Using plano-convex quartz resonators with higher Q value and higher driving levels, this acceleration can be much higher. Thus a quartz crystal resonator can create a megagravity field on its surface.

In order to evaluate the minimum detectable mass in the center of the quartz resonator, we used the frequency shift $\Delta f = 96.925\,Hz$ corresponding to the deposition of a silver spot with a mass $M_f = 3.3399 \times 10^{-10}\,kg$. The minimum detectable mass, M_f^{min}, also depends on the frequency stability, $\Delta f/f$, which can be attained over the length of the mass measuring process. Previously reported results (Warner and Stockbridge 1963), showed an experimental frequency stability of $\Delta f/f = \pm 1.5 \times 10^{-9}$ and stated that even $1\,pg/cm^2$ can be detected in case of a better temperature stability. This corresponds to a frequency stability of $\Delta f/f = 1.13 \times 10^{-11}$. In some special conditions (Vig and Walls 1994), using better temperature control and ultra-high vacuum we can rely on an even better frequency stability, $\Delta f/f = 5 \times 10^{-12}$. In this case $M_f^{min} = 8.53 \times 10^{-17}\,kg$. It is interesting

to look at the product between the minimum detectable mass and the acceleration acting on that mass:

$$\Gamma = M_f^{min} \cdot a_0 = 8.53 \times 10^{-17}\ \text{kg} \cdot 1.1238 \times 10^{7}\ \text{m/s}^2$$
$$= 9.5536 \times 10^{-10}\text{N} \approx 10^{-9}\text{N} \quad (5)$$

Conventional Microbalances

We can compare this result obtained for the case of the QCM with the case of the most sensitive balances we currently use in our laboratories: beam, cantilever, torsion, or spring balances. Depending on their maximum allowable load, the minimum detectable mass is $M_f^{min} = 0.1\,\mu g = 10^{-10}\,kg$. This sensitivity can only be attained in a vibration-free environment at a constant temperature.

All these balances have a common feature: the acceleration acting on the measured mass is just the gravitational acceleration, g. In this case we have $\Gamma = M_f^{min} \cdot g = 9.81 \times 10^{-10}\ \text{N} \approx 10^{-9}\,\text{N}$.

The Γ should not be interpreted as a universal constant. It is rather a proof that there is a connection between mass and acceleration. The magnitude of Γ refer to the same level of exigency towards the environmental conditions for both QCM and conventional balances. This idea was first discussed earlier (Mecea et al. 1996).

Acceleration Dependent Mass Sensitivity

On the surface of a quartz crystal resonator the acceleration of the shear vibration varies from zero to several millions times the gravitational acceleration, g, over a distance of 2 to 3 mm from about the electrode edges to the electrode center. The mass sensitivity varies in the same way.

The effect of the gravitational acceleration on the cantilever, torsion, and spring balances is obvious and will not be discussed here. However, a beam balance works as a comparator and it is interesting to take closer look at this type of balance.

In case of a beam balance with arms of equal lengths, the equilibrium is attained when $M_A \cdot g = M_B \cdot g$, where M_A and M_B are the masses of the bodies laid on the pans A and B, respectively, and g is the gravitational acceleration. We will have equilibrium when $M_A = M_B$, whatever the value of the acceleration is. The two bodies will be in equilibrium on both Earth and on the Moon. However, the mass sensitivity is not the same on Earth and on the Moon. In the general case, at equilibrium we have $M_A \cdot a = M_B \cdot a$, where a is the magnitude of the acceleration in that point. This is illustrated in Fig. 3.

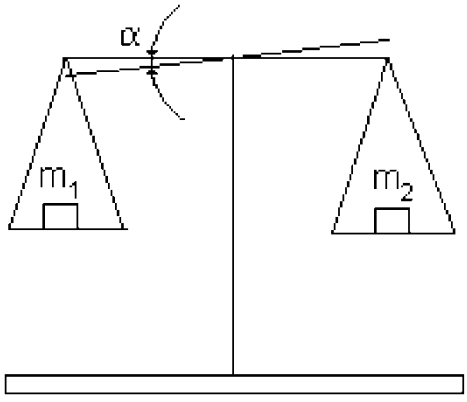

Figure 3. Mass sensitivity of a beam balance.

The balance sensitivity is measured by the tipping angle α, which corresponds to a small difference between the two masses. For small angles, α is proportional to the difference between the two forces acting on the two arms:

$$\alpha = \mathrm{k}\ (\mathrm{M_A} - \mathrm{M_B})\,\mathrm{a} \tag{6}$$

where k is a constant that depends on the mechanical construction of the balance. If $\alpha = 6^\circ$ on Earth, it will be only 1° on the Moon. None of the balances we normally use in our laboratories (beam, cantilever, torsion, or spring) can be used on a space laboratory orbiting around Earth, because the gravitational acceleration is canceled by the centrifugal acceleration. However, a QCM works excellently in outer space (Mecea 1994). The mass deposited on the surface of a quartz crystal resonator is subjected to an acceleration caused by the vibration of the quartz resonator.

The maximum value of the acceleration on the crystal surface can be increased by increasing the driving level in the crystal. However this will not increase the integral mass sensitivity of the crystal. The additional energy will be shared between quartz and the deposited film and the same fraction of vibration energy will be transferred to the film, whatever the driving level is. This is clearly stated in the Energy Transfer Model (Mecea 1994).

The value $\Gamma \approx 10^{-9}\,\mathrm{N}$ corresponds to very stable conditions. For a QCM this means ulta-high vacuum, constant temperature, no temperature gradients, and no stress inside the crystal resonator. For a laboratory balance this means constant temperature, no air convection, and no external vibrations. These provide an additional acceleration, which will be vectorially added to the gravitational acceleration.

EXPERIMENTAL EVIDENCE FOR THE PRESENCE OF A MEGA-GRAVITY FIELD ON THE SURFACE OF A QUARTZ RESONATOR

The experiments were performed using QCM-lab equipment with a specially designed oscillator, which permits a high drive level of the quartz resonators up to 150 mA. Using automatic level control (ALC) the crystal current could be scanned between 1 mA and 100 mA with different rates.

In these experiments six MHz, AT-cut plano-convex quartz resonators (Maxtek P/N 103200 and P/N 103218), with gold electrodes and a diameter of 14 mm were used.

The carbon-covered iron nanoparticles were deposited by an L-CVD (Laser assisted Chemical Vapor Deposition) system consisting of a vaporizing/sublimation chamber and a deposition chamber. An ArF excimer laser was used, operating at a wavelength of 193 nm, 50 Hz [nominal pulse duration: 15 ns (FWHM)] and a fluence of around 110 mJ/cm^2. The laser beam was focused with a cylindrical lens achieving a focusing area above the QCM-crystal of 0.13 cm^2 located at around 2 mm above the crystal.

The precursor ferrocene was vaporized/sublimated at a temperature of 43°C and introduced into the deposition chamber by the carrier gas, argon (Ar). The gas mixture of ferrocene and argon traveled parallel with the laser beam for 10 cm before reaching the deposition zone. Total pressure in the system was 30 mBar with a linear gas velocity of 8 cm/s. Most of the time the deposition time was 40 min.

In Fig. 4 a quartz resonator, which was coated with carbon nanoparticles for 40 minutes while the crystal current was 90 mA, is shown.

Although the laser beam was about 20 mm wide and the crystal was placed about 3 mm under the laser beam, the deposition was located only in

Figure 4. A 6 MHz plano-convex AT-cut quartz resonator coated with carbon nanoparticles for 40 minutes, while the crystal current was 90 mA.

the central part of the resonator where its vibration is located. This might be interpreted as sedimentation induced by the mega-gravity field of the shear vibrations in the center of the crystal. The deposition also revealed some parallel lines with significant difference in thickness. Those locations where the carbon film is thinner are regions where the crystal vibration has an out-of-plane component. At these locations the acceleration of the vibrations normal to the crystal surface is high enough to expel the carbon nanoparticles, which accumulate at the nodal locations. This experimental result is in accordance with the calculations made by EerNisse, Benes, and Schmid (2002) for flexural vibrations associated with the normal shear vibrations of the AT-cut resonators. The fact that deposition is located mostly in the central part of the resonator might be interpreted as a proof that shear vibrations induce sedimentation of the deposited carbon nanoparticles. It is a competition between sedimentation induced by shear vibrations and expelling induced by out-of-plane vibrations of the crystal. In Fig. 5 a resonator is shown that was coated with carbon nanoparticles while the crystal was placed 1 mm under the laser beam and the crystal current was 140 mA. It reveals two lobes, symmetrically positioned vs. the crystal centrum. The carbon-nanoparticles were also expelled because of the high acceleration. The amplitude of the out-of-plane vibrations in these regions is about 6% of the maximum amplitude of the shear vibration in the center of the crystal (Eer Nisse et al. 2002). The amplitude of the shear vibration can be calculated using the equation established by Borowsky, Mason, and Krim (2000). In our case it is about 100 million times higher than is the gravitational acceleration. Thus the acceleration of the out-of-plane vibrations in the region of the two lobes is about 6 million times higher than is the gravitational acceleration. This acceleration develops a force, normal to the crystal

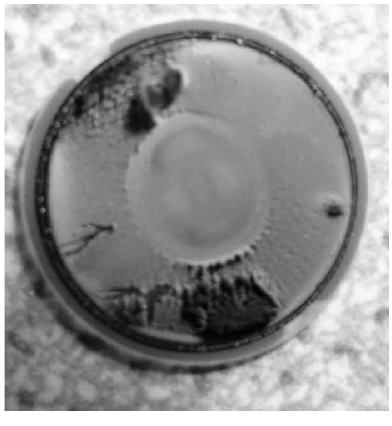

Figure 5. A 6 MHz plano-convex, AT-cut quartz resonator coated with carbon-nanoparticles while the crystal current was 140 mA.

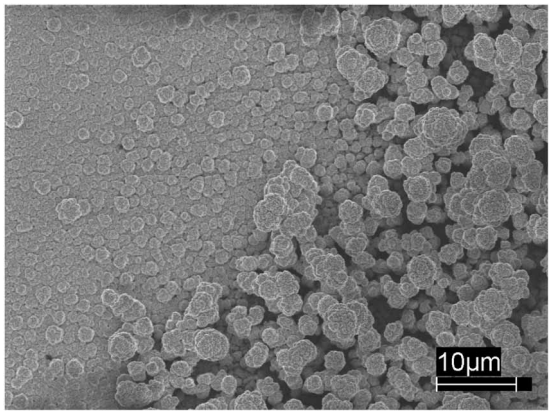

Figure 6. SEM picture of an area situated at the edge of one of the two lobes on the surface of the quartz resonator coated with carbon nanoparticles, the crystal current was 140 mA.

surface, which exceeds the binding force of the carbon-nanoparticles to the gold electrodes. In Fig. 6 a scanning electron microscope (SEM) picture of an area located at the edge of one of the two lobes is shown. This reveals the expelling of the carbon-nanoparticles agglomerates in the region with a high acceleration normal to the crystal surface.

The experimental results shown here reveal the complex situation on the surface of a shear vibrating quartz resonator used in QCM applications. The very high acceleration of the shear vibrations induces sedimentation of the C-nanoparticles, while the out-of-plane vibrations induce an expelling of the C-nanoparticles. In the early years of the QCM it was thought that AT-cut resonators exhibited a pure shear vibration. Later compressional waves were detected in liquids and the explanation was based on the existing velocity gradients in the contacting liquid (Martin and Hager 1989). The two lobes shown in Fig. 5 reveal that compressional waves are also produced by the crystal itself. In more recent research, the possibility for flexural vibrations was evidenced. This is slightly evident even in Fig. 4.

Thus, by coating a quartz resonator with C-nanoparticles it was possible to reveal the effects of the megagravity field.

FUNDAMENTAL PRINCIPLES OF MASS MEASUREMENTS

The equivalence principle, formulated by Einstein in 1907, states the equality of the gravitational and inertial masses. This is not only the basis for the theory of general relativity, but also has a direct consequence: if both a gravitational

field and an inertial field are present at a point of space, then the total acceleration is $\vec{a}_t = \vec{a}_g + \vec{a}_i$, where $\vec{a}_g$ is the gravitational acceleration and $\vec{a}_i$ is the inertial acceleration.

At a certain point of a gravitational field $\vec{a}_g$ has the same magnitude and direction.

At a certain point of an inertial field $\vec{a}_i$ can have a time-dependent magnitude and direction.

It is not possible to penetrate into a body, to identify all the atoms, and to add their masses in order to get the total mass of that body. One should use something that can act on a body from a distance, and this is the field. For a neutral body the field should be gravitational, inertial, or a superposition of these fields. For an electrically loaded body, the field can be electric or magnetic. In a mass spectrometer we need at least an electric field to measure the mass of the ions.

On the surface of a vibrating quartz crystal resonator we have an inertial field, its maximum intensity being at the center of the quartz resonator. The strong inertial field can be interpreted as a megagravity field. Here the sedimentation of even atoms and the development of anomalous phenomena is possible. A megagravity field may be useful in many applications in metallurgy, solid state chemistry, polymer physics, materials processing, or biochemistry.

Recently (Cooper et al. 2001; Dultsev et al. 2000), this mega-gravity field was used for the development of the so-called "bond breaking spectroscopy" and it might explain the enhanced catalytic activity on vibrating catalysts (Nishiyama et al. 1997; Kelling et al. 1997).

The inertial field developed at the surface of the QCM permits its use as a mass sensor in the outer-space on a space laboratory orbiting around the Earth although the gravitational acceleration is cancelled by the centrifugal acceleration (Mecea 1994).

The QCM is not only a mass sensor, but also an actuator, providing a megagravity field on its surface.

It doesn't matter what the vibrational mode of the quartz resonator is, in order to be used as a mass sensor (Benes et al. 1995; Martin et al. 1998; Mecea 1994; Wenzel and White 1989).

It doesn't matter if we use quartz or other piezoelectric material for mass sensing (Fritze et al. 2001; Mecea 1994; O'Toole et al. 1992).

The only important thing is to provide an acceleration to the body who's mass we want to measure.

QCM RESPONSE IN A LIQUID

The concept of an acceleration-dependent mass sensitivity can explain why the frequency of a shear vibrating quartz crystal resonator, in contact with a liquid, depends on the viscosity of the liquid.

The frequency change, when one face of a quartz crystal resonator is in contact with a liquid with density ρ_l and viscosity η_l, was first calculated by (Kanazawa and Gordon 1985) and later using the Energy Transfer Model (Mecea 1994).

$$\Delta f = -f_q^{3/2}\left(\frac{\rho_l \eta_l}{\pi \rho_q \mu_q}\right)^{1/2} \tag{7}$$

where ρ_q and m_q are the quartz density and shear modulus, respectively.

When such a resonator is in contact with a liquid, and this is a common situation in many applications of the QCM, the vibration amplitude, and also the acceleration, decay exponentially from the crystal surface into the liquid, as shown in Fig. 7.

$$A(y) = A_0 \exp(-y/\delta) \tag{8}$$

where $\delta = (\eta_l/\pi f_q \rho_l)^{1/2}$ is the penetration depth, defined as the distance into the liquid layer where the vibration amplitude has diminished e times. Here η_l and ρ_l are the liquid viscosity and density respectively, and f_q is the quartz resonator frequency. A_0 is the maximum vibration amplitude at the center of the crystal resonator.

The larger the distance y from the quartz-liquid interface, the lower the vibration amplitude and acceleration. A certain small volume of liquid situated at distance δ from the quartz-liquid interface will produce a frequency change e-times smaller than that produced by the same volume of liquid situated in direct contact with the quartz surface. Because the mass sensitivity is acceleration dependent, it is obvious that the mass sensitivity depends on both the liquid density and viscosity. Liquid viscosity determines the amplitude and acceleration decaying profile. It is a widespread opinion that QCM is not only sensitive to the density of the contacting liquid, but also to the viscosity of this liquid (Henry 1996). This is true, but it is a second

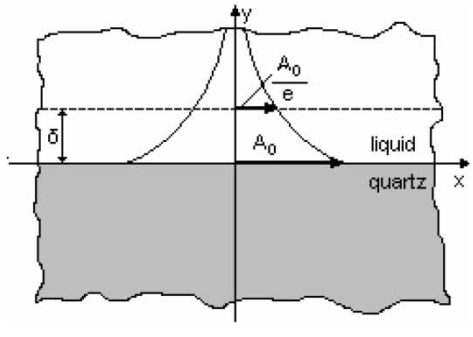

Figure 7. Amplitude and acceleration decay at the quartz-liquid interface.

order effect. The prime effect is an acceleration-dependent mass sensitivity and acceleration, as well as vibration amplitude, follows a function that includes both the liquid viscosity and density, as illustrated in Fig. 7. It is interesting to notice that in Eq. (7) we have the product between density and viscosity under square root. The two physical quantities can not be separated. It should be a mechanism that is binding them together. This is the acceleration-dependent mass sensitivity.

The film deposited on the quartz resonator surface must be adherent to the quartz resonator surface in order to have the same acceleration as the quartz resonator.

When the quartz resonator is in contact with a liquid, its roughness, or crevices can trap liquid molecules that will vibrate with the same amplitude and acceleration as the quartz resonator surface. These trapped molecules will exhibit a solid film behavior, producing an additional frequency change (Martin et al. 1991; Theisen et al. 2004).

CONCLUSIONS

The QCM is not only a sensitive mass sensor but it is also an actuator generating a megagravity field on the surface of the quartz resonator. The very high mass sensitivity of the QCM is explained by the very high acceleration acting on the deposited film.

The product between the minimum detectable mass and the acceleration acting on that mass is a constant for both QCM and analytical microbalances when equivalent experimental conditions are used. For best experimental conditions this constant has a value of about 10^{-9} N.

Acceleration is a paramount condition for mass measurement. Therefore, in order to measure the mass of a body, we must place that body in a field.

The viscosity-dependent frequency change of a quartz resonator in contact with a liquid is a second order effect resulting from the acceleration-dependent mass sensitivity of the QCM.

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